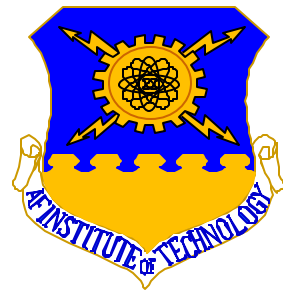AFIT/EN/TR-02-05
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Treatment of chlorinated aliphatic contamination of groundwater by horizontal recirculation wells and by constructed vertical flow wetlands

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Abstract
This work explores two innovative technologies for the remediation of chlorinated ethene solvents contaminating groundwater: 1) groundwater circulation wells (GCWs) with downwell zero-valent metal reductive dechlorination reactors and 2) constructed vertical subsurface flow wetlands. Both the natural dechlorination in wetland sediments, and the engineered dechlorination in a well using zero-valent metals have major implications for the treatment of Air Force pollutants, with the potential to save millions of dollars annually in long term remediation at hundreds of sites across the Air Force. Complementary modeling and column studies examined the potential for controlling and treating groundwater contamination using groundwater circulation wells (GCWs) with downwell zero-valent metal reductive dechlorination reactors. The construction of the field scale wetland research facility includes two complete wetland cells (140x60 feet each), fully contained. Chemical analysis of samples drawn from the various depths of wetland sediment suggests a very heterogeneous development of microbial activity relevant to reductive dechlorination over the course of one year of operation. Concentration contours of PCE, TCE, and nitrate suggest that reductive dechlorination is taking place when more readily reducible electron acceptors (like nitrate) are depleted. PCE is reduced ten-fold from inflow to outflow, even with significant short-circuiting of flow from the bottom sediments to the outflow. Data suggests 100-fold treatment is possible.

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FINAL REPORT
Dayton Area Graduate Studies Institute

Project Nr.: **ML-AFIT-99-06**   **Lead Institution:** **AFIT**

Project Title: **Abiotic and Biochemical Fate &** **Partner(s):** **WSU**
      Transport of Contaminants

Team Leader: Dr. Mike Shelley

EXECUTIVE SUMMARY

This work explores two innovative technologies for the remediation of chlorinated ethene solvents contaminating groundwater: 1) groundwater circulation wells (GCWs) with downwell zero-valent metal reductive dechlorination reactors and 2) constructed vertical subsurface flow wetlands. Both the natural dechlorination in wetland sediments, and the engineered dechlorination in a well using zero-valent metals have major implications for the treatment of Air Force pollutants, with the potential to save millions of dollars annually in long term remediation at hundreds of sites across the Air Force. Strong collaborative funding from the Dayton Area Graduate Studies Institute (DAGSI) and the Defense Environmental Restoration Account (DERA) created a center of field and laboratory research for ecological and remediation engineering, integrating already active research teams from Wright State University (WSU) and the Air Force Institute of Technology (AFIT).

On-going, long term remediation projects designed to clean up groundwater contamination are costing the Air Force and DOD millions of dollars every year in operations costs with little hope of successful completion in the foreseeable future. Chlorinated solvent plumes, in particular, must be captured and remediated before they move with groundwater flow across base boundaries and present an exposure risk to receptors beyond the installation. Although there are some innovative in situ technologies that have been effective in destroying the contaminants within the subsurface, the most universally reliable technique for plume control is well extraction of large volumes of groundwater in front of the plume, sufficient to "capture" any flowing groundwater laden with contaminants. Once the contaminated water is at the surface, it must be treated for contaminant destruction, generally by expensive, energy-intensive thermal or controlled biological processes prior to discharge. Moreover, intercepting the contaminant at the forward boundary of the plume (even if the upstream source of contamination is eliminated) will require years or decades of pumping and treating due to the continual adsorption and desorption of these chlorinated organics to and from the soil. Large volumes of water with very dilute concentrations must be continually pumped to eventually purge the soil of all contaminant. Annual operating costs of a single such

system can be millions of dollars, most of which is spent in the treatment phase after pumping.

Complementary modeling and column studies examined the potential for controlling and treating groundwater contamination using groundwater circulation wells (GCWs) with downwell zero-valent metal reductive dechlorination reactors. A battery of wells is arrayed ahead of the advancing contaminant plume not unlike a battery of extraction wells designed for plume capture in a conventional pump-and-treat scheme. However, instead of extracting water, the well pumps and screens are designed to pump both out of and into the saturated zone to create a circulating pattern. The number of wells, pumping rate, and screen placement is designed to capture the entire plume within the circulation and provide for sufficient passes through the in-well reaction beds to destroy contaminants prior to the flowing groundwater escaping the circulation pattern and moving down-gradient. The reaction beds provide surface exposure to zero-valent metals that catalyze the dechlorination of chlorinated ethenes in the presence of hydrogen. In conjunction with the laboratory studies conducted at Wright State University, AFIT developed a model of Palladium (Pd)-catalyzed dehalogenation. The model simulates Pd-catalyst deactivation by multiple poisons, as well as catalyst regeneration. This model was coupled with simulation of a GCW system. Applying the model under realistic conditions showed that the GCW system could operate approximately 130 days without significant catalyst deactivation. This suggests catalyst deactivation may not significantly affect operating costs or system performance in a real remediation scenario. The model improves our understanding of the processes affecting treatment efficiency and represents an important step in transitioning the technology to field application.

A controlled laboratory approach was completed for studying the reaction kinetics of contaminants in the presence of a catalyzing metal surface. Batch studies have determined contaminant degradation rate constants under varying conditions. The batch studies demonstrated that degradation of chlorinated ethenes using a Pd catalyst was extremely rapid and that a Pd catalytic reactor could potentially be used as a component in an in-well flow through system. Complete degradation of chlorinated ethenes has been clearly demonstrated without the addition of energy to the process. In a series of column studies, WSU evaluated the factors affecting dehalogenation rates for trichloroethylene, perchloroethylene, and three dichloroethylene isomers using supported Pd catalysts with hydrogen gas, studying the effect of flow rate, substrate concentration, catalyst bed configuration, and catalyst deactivation by sulfide and chloride ions, etc. upon dehalogenation kinetics. The column studies indicated that reaction kinetics transition from Michaelis-Menten type behavior to first-order as the ratio of catalyst to contaminant increases.

With regard to field-testing of the technology, the Department of Defense Environmental Security Technology Certification Program (ESTCP) agreed to fund a two-year field evaluation of the technology. Preliminary work began in 2001, with site construction scheduled to commence in July 2002 at Edwards AFB in California.

The wetlands research hypothesizes that constructed wetlands can be used to successfully treat groundwater contamination by naturally occurring processes with little cost and that these processes can be modeled and enhanced through engineering intervention. The mechanism of this accelerated degradation in and/or near wetlands is hypothesized to be unique microbial as well as abiotic processes made possible by the highly chemically reducing environment created in the organic-rich wetland sediment. This dynamic and productive region (interacting with the highly productive plant life typical of wetlands) continually supplies the nutrients which keep these processes highly active (in contrast to normal subsurface groundwater conditions). Low concentrations of even slowly degrading compounds like TCE can potentially be reduced to zero in these environments very quickly. Methanogenic conditions typically prevail in fresh water wetland sediments (active microbial populations producing methane) using carbon dioxide as the terminal electron acceptor in energy producing metabolism. Since halogenated organics like TCE serve as better electron acceptors than CO_2, they are quickly destroyed in this active environment. The engineering concept is to distribute contaminated water into well-defined wetland sediment regions in a uniform and sequential flow scheme to effect an overall efficient and reliable treatment that completely destroys or lowers contaminant concentrations to designed levels. This is best achieved by introducing water below the region of wetland influence and providing for uniform upward flow through uniform sediment layers of designed characteristics.

Systems modeling of a constructed vertical flow wetland was completed which ties together the various processes occurring within wetland sediments and their influence on each other. It is structured to simulate the engineering design of the constructed field cell phase of the work. Results point to the importance of the ability of plants to drive oxygen into the root zone of the soil as well as the importance of optimizing microbial metabolic activity related to contaminant destruction (both reductive dechlorination and oxidative destruction). Model results show that hydrogen (a major product of natural organic matter breakdown) plays the dominant role in both methane production and dechlorination of the contaminants. Certain levels of hydrogen may favor methane production over dechlorination while lower levels of hydrogen may favor dechlorination over methanogenesis. This poses an interesting optimization problem in that dechlorination is the primary objective in the lower region of sediment, but methane production is also desired for flow to and use in the top layer as part of the envisioned sequential degradation of contaminants.

Laboratory flask, small column, and greenhouse experiments were conducted to test the methane generation potential of various soils (some amended with composted organic material) collected from historical natural wetland areas. Microcosm bench studies have defined field conditions that will optimize methane generation. Separate plant species studies were conducted to determine differential ability to foster methane oxidation within the root zone just below the surface (consistent with the engineering design concept). Plants differentially force oxygen into the soil and provide conditions for aerobic microbial populations to oxidize methane as a primary food source (and low levels of contaminants as a secondary food source). Data have shown no statistical difference among the species tested in ability to oxidize methane in aerobic conditions or

produce methane in anaerobic conditions. Bench level microcosm soil studies evaluated the potential of naturally occurring microorganisms in the destruction of perchloroethylene and its degradation products. Soil from a drained wetland was used in microcosms to assess the ability of a naturally occurring microbial consortium, having no previous exposure to chlorinated ethylenes, to reductively dechlorinate perchloroethylene to a harmless end product. Long term studies (6 months) revealed PCE dechlorination, in the presence of abundant methanogenesis, with cis-DCE as the major transformation product. These results confirm that additional oxidative destruction of DCE may be important in layers above a highly reducing sediment layer. Results also suggest that the indigenous microbes are capable of PCE dehalogenation to ethene, although complete dechlorination is relatively slow. Follow-on column studies, using trichloroethene (TCE) as a contaminant, demonstrate a hundred fold decrease in TCE from the bottom to the top of the upward flow column. No intermediate degradation products have been detected, suggesting that TCE (and intermediate products) is either completely oxidized to carbon dioxide or bound within the soil matrix of the column. Strong binding within the soil is consistent with expectations and is considered a favorable phenomenon for optimization of treatment in the field. Root zone column studies also demonstrated as much as 50% evapotranspiration (50% of the water flow transported to the atmosphere through the plant leaves) at the flow rates used. This phenomenon would effectively remove the contaminants from the water flow and would either destroy the contaminant by natural plant metabolic processes or transfer the contaminant to the atmosphere along with the water. Given the apparent strength of this process, a strong line of research is indicted to explore this phytoremediation effect in both natural and constructed wetlands. Continued column studies in this project determined the partitioning of treated contaminant among anaerobic reductive dechlorination, aerobic oxidative destruction, removal from the water by binding to soil, and phytoremediation processes. C-14 labeled contaminants were used to trace their fate.

The construction of the field scale wetland research facility includes two complete wetland cells (140x60 feet each), fully contained, under Ohio EPA Permit to Install # 05-10719. Construction broke ground in Nov 99 and was completed in Jan 00 ready for Spring planting. The field site consists of two parallel lined cells with controlled inflow and outflow and complete containment. A source of PCE contaminated groundwater lies beneath. Cells are independent and isolated to support controlled experiments. Multi-level transect sampling grids are installed using drive point piezometers. Samples derived from the piezometers monitor initial and developing physical, chemical, and biochemical conditions of the wetland soils as well as contaminant and contaminant breakdown products at multiple depths across the wetland area. Piezometers were also used to develop piezometric head contours and estimates of hydraulic conductivity though out the wetland sediment.

Chemical analysis of samples drawn from the various depths of wetland sediment suggests a very heterogeneous development of microbial activity relevant to reductive dechlorination over the course of one year of operation. Concentration contours of PCE, TCE, and nitrate suggest that reductive dechlorination is taking place when more readily reducible electron acceptors (like nitrate) are depleted. PCE is reduced ten-fold from

inflow to outflow, even with significant short-circuiting of flow from the bottom sediments to the outflow. Data suggests 100-fold treatment is possible. No mass balance of contaminants and their degradation products is possible (no chlorinated species below TCE are detected), suggesting that much of the input PCE continues to reside in the system, likely sorbed to the highly organic soil.

Follow on work is in progress, analyzing further development of the system over another year of operation.

Reporting Period: July 1, 1999 through January 31, 2002

FINAL REPORT
Dayton Area Graduate Studies Institute

Project Nr: <u>ML-AFIT-99-06</u>   **Lead Institution:** <u>AFIT</u>

Project Title: <u>Abiotic and Biochemical Fate &</u>   **Partner(s):**   <u>WSU</u>
                <u>Transport of Contaminants</u>

Team Leader: <u>Dr. Mike Shelley</u>

BACKGROUND

On-going, long term remediation projects designed to clean up groundwater contamination are costing the Air Force and DOD millions of dollars every year in operations costs with little hope of successful completion in the foreseeable future. Chlorinated solvent plumes, in particular, must be captured and remediated before they move with groundwater flow across base boundaries and present an exposure risk to receptors beyond the installation. Although there are some innovative *in situ* technologies that have been effective in destroying the contaminants within the subsurface, the most universally reliable technique for plume control is well extraction of large volumes of groundwater in front of the plume, sufficient to "capture" any flowing groundwater laden with contaminants. Once the contaminated water is at the surface, it must be treated for contaminant destruction, generally by expensive, energy-intensive thermal or controlled biological processes prior to discharge. Moreover, intercepting the contaminant at the forward boundary of the plume (even if the upstream source of contamination is eliminated) will require years or decades of pumping and treating due to the continual adsorption and desorption of these chlorinated organics to and from the soil. Large volumes of water with very dilute concentrations must be continually pumped to eventually purge the soil of all contaminant. Annual operating costs of a single such system can be millions of dollars, most of which is spent in the treatment phase after pumping.

The technologies presented in this work recognize the need to pump groundwater to control contaminant migration while exploring more cost effective means of contaminant destruction once pumped. Two such means of treatment (explored here) are 1) groundwater circulation wells (GCWs) with downwell zero-valent metal reductive dechlorination reactors and 2) constructed vertical subsurface flow wetlands. Both the natural dechlorination in wetland sediments, and the engineered dechlorination in a well using zero-valent metals have major implications for the treatment of Air Force pollutants, with the potential to save millions of dollars annually in long term remediation at hundreds of sites across the Air Force. Natural attenuation and *in situ* destruction are fast becoming the regulatory agencies' preferred method of pollution abatement over other alternatives when technologically feasible. Incineration is costly and often produces undesirable by-products such as dioxins. Air stripping and adsorption technologies simply change the phase of the contaminant and dilute it into other media (e.g. air) or concentrate it for follow-on destruction.

A number of groundwater plumes of chlorinated solvents were discovered beneath Air Force bases in the late 1970's, and, after years of intense investigation, the problem is now endemic across the Air Force. Lower molecular weight chlorinated hydrocarbons, particularly trichloroethylene (TCE), were used as solvents in routine maintenance of weapon system components on most flightlines and were stored in bulk using large tanks, often underground. Solvent use and storage practices today prevent leakage into the ground, but practices from 20 and 30 years ago still pose a threat to public health, ecosystem viability, and defense environmental budgets due to the very long persistence of these compounds in the environment once released. TCE, in particular, will migrate downward to the bottom of a groundwater aquifer and become a long term source of spreading environmental contamination for decades. Dissolving into slowly moving groundwater, it continues to sorb onto and de-sorb from soil, "smearing" contamination within the aquifer for miles while being very resistant to natural degradation processes which would easily act on non-chlorinated petroleum hydrocarbons. Millions of dollars are spent annually in the Air Force every year in a continual effort to prevent migration of such contamination outside base boundaries (usually plume capture by extraction wells and subsequent destruction of the TCE once pumped out of the ground). These annual expenditures continue for years (decades) awaiting technology breakthroughs which will allow a quicker, permanent, and cheaper solution. Air Force environmental technology research expenditures have been predominantly focused in this area over the past 15 years. Research has migrated toward identifying and enhancing processes that destroy the contaminant in the ground, or in-situ. Even after years of research, however, there are still only three primary strategies that are used to contain the transport of groundwater contaminated by chlorinated hydrocarbons: (1) pump-and-treat, (2) natural attenuation, and (3) treatment walls. Unfortunately, pump-and-treat involves the increased cost and risk of pumping contaminated water to the surface, natural attenuation is typically inadequate (in rate and/or extent) to adequately treat chlorinated compounds, and treatment walls only work under very specific hydrogeologic conditions (relatively shallow water table, no seasonal fluctuations in groundwater flow direction, etc.). The research proposed here will use an existing groundwater plume at Wright-Patterson AFB to investigate and develop the two alternative groundwater treatment strategies.

This work directly addresses AFRL/MLQ's mission area of environmental security and establishes a team effort that plays on the strengths of existing research groups at Wright State University (WSU) and the Air Force Institute of Technology (AFIT). Researchers at AFRL/MLQ and Wright State University have been among the leaders in the development of zero-valent metal reductive dechlorination to treat groundwater contaminated with chlorinated compounds. This technology has typically been applied using treatment walls--essentially trenches through which contaminated groundwater passes. Unfortunately, these treatment walls can only be used under specific hydrogeologic conditions (e.g. relatively shallow and steady contamination zones). Recent field work involving AFIT has looked at the possibility of *in situ* treatment using groundwater circulation wells (GCWs). The use of zero-valent metal reductive dechlorination in a GCW (metal enhanced GCW system) is studied here. Metal enhanced GCWs have the advantages of treatment walls (*in situ* destruction of contaminant) while

avoiding the disadvantages, allowing positive control of contaminant migration at depth).

Wright State University has a long and well published history of field scale wetland development and experimentation as well as experimental work in aquatic sediment processes and contaminant effects. AFIT currently publishes work in system dynamics modeling of wetland systems and their optimization for assimilation of contaminant discharges as well as subsurface contaminant fate and transport (with Wright State) including abiotic and biochemical transformations. This unique blending of engineering modeling with principles of ecological systems experimentation builds a focused interdisciplinary team not seen at most other research centers. The team explores the concept of constructed wetlands as a pump-and-treat system offering a very low cost treatment at the surface with reliable plume control at depth.

Some contaminant groundwater plumes are shallow and intersect wetland ecosystems on the surface in accordance with natural groundwater flow. Observations of these systems, when they are found, suggest an accelerated natural degradation of these otherwise slow degrading compounds. The most striking example is Aberdeen Proving Grounds where measurements taken indicate complete destruction (reduction of TCE to non-detectable levels) by natural attenuation within the zone of wetland influence with no engineering enhancement. This is supported by substantial bench level work which shows that reductive biodegradation (dominant in freshwater wetland sediments) completely dechlorinates heavily chlorinated ethenes much more rapidly than any other naturally occurring process. Additional work at AFRL/MLQ indicates significant abiotic reductive dechlorination in humic soils typical of wetland sediments. AFRL/MLQ is preforming a three year project ($1.1M, Environmental Security Technology Certification Program) to investigate conditions at five sites where contaminant solvent plumes are intersecting existing wetlands (including Aberdeen). The work involves installation of multi-level transect sampling of existing conditions to determine and document operating natural attenuation processes and degree of attenuation taking place. The data being gathered is designed to determine groundwater flow paths; determine regions of changing redox potential as created by the wetland sediment system; evaluate contaminant destruction through measurements of the primary contaminant, reactive intermediates, and non-toxic end products; and differentiate biotic and abiotic processes. This empirical data, gathered at naturally occurring sites, will allow the formation of hypotheses concerning contaminant destruction mechanisms based on correlation of chemical conditions with contaminant concentrations at multiple sites with varying characteristics. These concepts can then be developed into design parameters for constructed wetlands after optimization using the constructed wetland cells employed here along with supporting laboratory and modeling work.

In order to confirm and/or refine mechanistic concepts arising from the field data collected by AFRL, modeling and controlled experimentation on an ecologically viable scale is required. The field data should point to specific sediment/sub-surface chemical conditions which appear to provide optimum degradation rates under specific site conditions. These chemical conditions arise from natural wetland processes which are

dynamic and involve a complicated set of ecosystem interrelationships. Sediment and its chemical characteristics change with ecosystem succession, developing richer organic and nutrient content with time and with successional variation of dominant species. The scope of these long term changes is not apparent over short term observations. Also not available with the AFRL field data is knowledge of previous conditions prior to contamination and possible increasing inhibition of critical ecosystem processes as a result of the presence of contamination. Knowing these trends would give insight into the long term sustainability of these systems in continuing to treat contamination by natural attenuation as well as possible compliance issues associated with degradation of the wetland. Complete investigation of these issues is possible only under conditions of controlled experimentation at an ecosystem scale such as that provided by a constructed wetland with controlled addition of contaminant and well designed monitoring strategies presented in this work. Knowledge of wetland processes can be modeled using a system dynamics analysis approach to simulate trends of developing characteristics which are consistent with field observations. Simulated trends then guide controlled experiment design which will yield data directly relevant to assumed significant processes and hypothesized contaminant mechanisms. Time course trends in the controlled experiment data will guide refinement of model structure. Validated model structure can be used in the design of sustainable optimum treatment configurations to be tested under controlled conditions and then demonstrated full scale.

The research group for this work is a multidisciplinary team that includes scientists with expertise in microbiology, geosciences, aquatic sediment biology, wetland ecology, aquatic chemistry, mathematical modeling, and systems analysis. The faculty team led 9 graduate students from both WSU and AFIT through to completion of their degrees from this project.

TECHNOLOGY CONCEPT

GCW Reductive Dechlorination Reactors. Complementary modeling and column studies examined the potential for controlling and treating groundwater contamination using groundwater circulation wells (GCWs) with downwell zero-valent metal reductive dechlorination reactors. Figure 1 demonstrates the engineering concept.
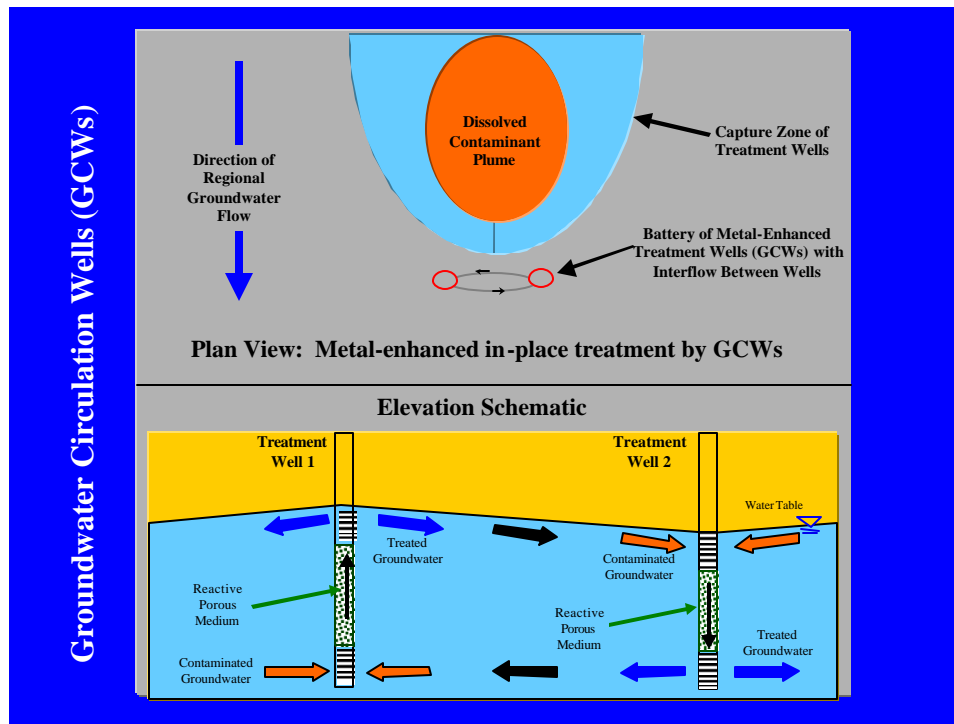
Figure 1. Plan and elevation views of plume capture and subsurface circulation with in-well treatment.

As illustrated, a battery of wells is arrayed ahead of the advancing contaminant plume not unlike a battery of extraction wells designed for plume capture in a conventional pump-and-treat scheme. However, instead of extracting water, the well pumps and screens are designed to pump both out of and into the saturated zone to create a circulating pattern. The number of wells, pumping rate, and screen placement is designed to capture the entire plume within the circulation and provide for sufficient passes through the in-well reaction beds to destroy contaminants prior to the flowing groundwater escaping the circulation pattern and moving down-gradient. The reaction beds provide surface exposure to zero-valent metals that catalyze the dechlorination of chlorinated ethenes in the presence of hydrogen. Design optimization issues include the type of metal, metal surface geometry, hydrogen addition, reaction rates, and pumping rates consistent with plume capture and efficient treatment.

Constructed Vertical Flow Wetlands. The hypothesis is that constructed wetlands can be used to successfully treat groundwater contamination by naturally occurring processes with little cost and that these processes can be modeled and enhanced through engineering intervention. The mechanism of this accelerated degradation in and/or near wetlands is hypothesized to be unique microbial as well as abiotic processes made possible by the highly chemically reducing environment created in the organic-rich wetland sediment. This dynamic and productive region (interacting with the highly productive plant life typical of wetlands) continually supplies the nutrients which keep these processes highly active (in contrast to normal subsurface groundwater conditions). Low concentrations of even slowly degrading compounds like TCE can potentially be

reduced to zero in these environments very quickly. Methanogenic conditions typically prevail in fresh water wetland sediments (active microbial populations producing methane) using carbon dioxide as the terminal electron acceptor in energy producing metabolism. Since halogenated organics like TCE serve as better electron acceptors than CO_2, they are quickly destroyed in this active environment.

Very few contaminant groundwater plumes intercept wetlands on the surface. Most must be intercepted by engineering intervention, usually extraction wells, to prevent further migration down gradient. Once extracted (or momentarily sequestered in the subsurface), the contaminant must be separated from the water (and subsequently destroyed) or treated in the water phase prior to discharge of the water on the surface or back to the groundwater aquifer. Wetlands (natural or constructed) offer a mechanism of aqueous phase treatment at no additional cost while providing other environmental benefits usually associated with viable wetlands (including wetland mitigation or banking which may be required for environmental compliance). (Pumping to capture groundwater plumes often lowers the water table and endangers existing wetlands in the area).

Co-metabolic reduction reactions that degrade chlorinated solvents occur in anaerobic conditions. In these anaerobic conditions, certain bacteria such as methanogens and sulfate-reducers are able to reduce PCE and TCE (Bagley and Gosset, 1989). The reactions undertaken by these types of bacteria is considered to be co-metabolic rather than energy-yielding because only a fraction of the total reducing equivalents derived from the oxidation of electron donors is used to reduce the solvent (Bagley and Gosset, 1989). Reduction of chlorinated solvents appears to be a minor by-product in these cases. However, in situations where high organic levels and high methanogenic respiration are found, such as wetland sediments, the partial co-metabolic dechlorination of solvents can be significant (Lee et al, 1997).

Energy-yielding solvent oxidation reactions occur in situations where microbes use the chlorinated solvent as the sole source of carbon and energy. As the name suggests, these reactions may take place in areas where oxygen is readily available, such as the root zone of wetland sediment. However, research has shown that these reactions may occur in anaerobic conditions as well. Under aerobic and some anaerobic conditions, the less-oxidized chlorinated aliphatic hydrocarbons (VC, DCE) can be used as the substrate (electron donor) in biologically mediated redox reactions (Weidemeier et al, 1997). This process is probably restricted to the fringe of contaminant plumes because readily oxidizable substrates and oxygen rarely co-occur within the core of mature contaminant plumes. An example of this reaction is the conversion of 1,2-DCE to carbon dioxide by certain aerobic bacteria in streambed sediments. Experiments showed that the microorganism community in the sediment was able to fully eliminate 1,2-DCE when no other sources of carbon were present. Although no microbial growth was observed during the experiment, studies suggest that growth would occur in the presence of greater contaminant concentrations. This suggests that DCE can be degraded as the primary substrate in microbial metabolism and that this process may contribute to the natural attenuation of DCE even under circumstances where aerobic cometabolism is not favored (Bradley and Chapelle, 2000).

Energy-yielding reduction reactions or halorespiration is the process by which microorganisms are capable of using PCE or TCE as electron acceptors for biologically useful energy generation. These microorganisms are distinct from the co-metabolic reactions found among the methanogens and sulfate-reducers. Depending on the species of microbes present, these bacteria may produce cis-DCE as a final end product or may carry out complete dechlorination to ethane (Lee et al, 1997). These microbial processes show that oxygen need not be present for complete mineralization of chlorinated solvents. They further suggest that because of the energy yielding nature of the reactions, chlorinated solvent plumes may be self-enriching for dehalogenating bacteria. That is, the flowing contaminated groundwater continues to supply the electron acceptors necessary for microbial growth (Lee et al, 1997). Hydrogen and simple organic compounds are typically seen as the electron donors in these reactions.

In aerobic conditions, VC can be oxidized directly to carbon dioxide and chloride. At the interface between aerobic and anaerobic microenvironments, where methane and oxygen are both available, cometabolic oxidations can convert chlorinated ethenes to carbon dioxide and chloride. In anaerobic environments where electron donors such as organic carbon or hydrogen are present, reductive dehalogenation is the predominant mechanism (Lee et al, 1997).

Rapid microbial mineralization of VC has been observed in laboratory cultures and aquifer samples under aerobic conditions and in systems enriched with methane and oxygen. Because of this, it has been suggested that sequential anaerobic/aerobic biodegradation by indigenous microorganisms may be an effective means of bioremediating aquifers contaminated with chlorinated ethenes (Vogel, 1994). However, the addition of oxygen to groundwater to stimulate biodegradation is expensive and in many cases impractical (Bradley and Chapelle, 1996).

In contrast to reactions in which the chlorinated hydrocarbon is used as an electron acceptor (see energy-yielding reduction reactions above), only the least oxidized chlorinated aliphatic hydrocarbons (VC and DCE) can be used as electron donors in biologically mediated redox reactions. For example, PCE is fully chlorinated and does not serve as an electron donor for aerobic or anaerobic microbial consortia (Lee et al, 1997). TCE, however, is able to give up one electron and is able to be reductively dechlorinated (co-metabolic reduction). McCarty and Semprini (1994) describe investigations in which VC and 1,2-dichloroethane were shown to serve as primary substrates under aerobic conditions. In addition, Bradley and Chapelle (1996) show evidence of mineralization of VC under iron reducing conditions so long as there is sufficient bio-available $Fe(III)$ (Wiedemeier et al, 1997).

Wetlands hold properties that make them unique among major ecosystem groups on the earth. They have a higher rate of biological activity than most other ecosystems. Because of this, they are able to transform many of the common pollutants that occur in conventional wastewater (or groundwater) into harmless byproducts or essential nutrients that can be used for additional biological productivity (Kadlec and Knight, 1996). This

capacity for transforming contaminants has led to research into using constructed wetlands as a means of removing contaminants from both surface wastewater and subsurface groundwater flows. Natural attenuation of chlorinated solvents within subsurface groundwater is very slow. It is often so slow that long plumes of contaminant are generated that can reach surface discharge sites such as wetlands (O'Loughlin and Burris, 1999). Recent studies have detailed the effect that a freshwater tidal wetland had on an aquifer contaminated by PCE at Aberdeen Proving Ground in Maryland at the head of Chesapeake Bay (Lorah and Olsen, 1999). Results at Aberdeen indicate that natural attenuation processes increase dramatically as contaminated groundwater passes through the root zone of a wetland system. Rate constants of 30-40 year^{-1} have been observed for dechlorination of TCE in wetlands as opposed to 1-4 year^{-1} that is typically found in non-wetland contaminated aquifers (Pardue et al, 2000).

One of the first demonstrations of using wetland sediments to remove chlorinated solvents via reductive dechlorination was performed using sediment from the Everglades in south Florida (Parsons and Lage, 1985). The studies identified the dechlorination kinetics of PCE, TCE, and other chlorinated solvents. The conclusions of these studies are that wetlands are ideal environments for reductive dechlorination processes (Pardue et al, 2000). Additional research of the root zone associated with wetland plants demonstrated that the biodegradation of chlorinated organics in the region directly adjacent to plant roots can be dramatically higher than in bulk soil (Anderson and Walton, 1995). A key mechanism in this degradation is the co-metabolism of chlorinated solvents and daughter products by methanotropic organisms that function under aerobic conditions using methane as an electron donor (Pardue et al, 2000). This process was described in detail earlier in this chapter. The process was confirmed by laboratory work performed by Lorah and Olsen in 1999.

Use of wetland systems for contaminant treatment requires an understanding of the dominant processes involved and the characteristics of those processes which favor contaminant destruction. It is expected that distribution of extracted contaminated groundwater into a well designed constructed wetland system will provide complete destruction of contaminant over the long term with little to no cost except that required to monitor the process. The engineering concept is to distribute contaminated water into well-defined wetland sediment regions in a uniform and sequential flow scheme to effect an overall efficient and reliable treatment that completely destroys or lowers contaminant concentrations to designed levels. This is best achieved by introducing water below the region of wetland influence and providing for uniform upward flow through uniform sediment layers of designed characteristics. Figure 2 conceptually demonstrates one such design (the as-built design of one constructed cell in this effort).
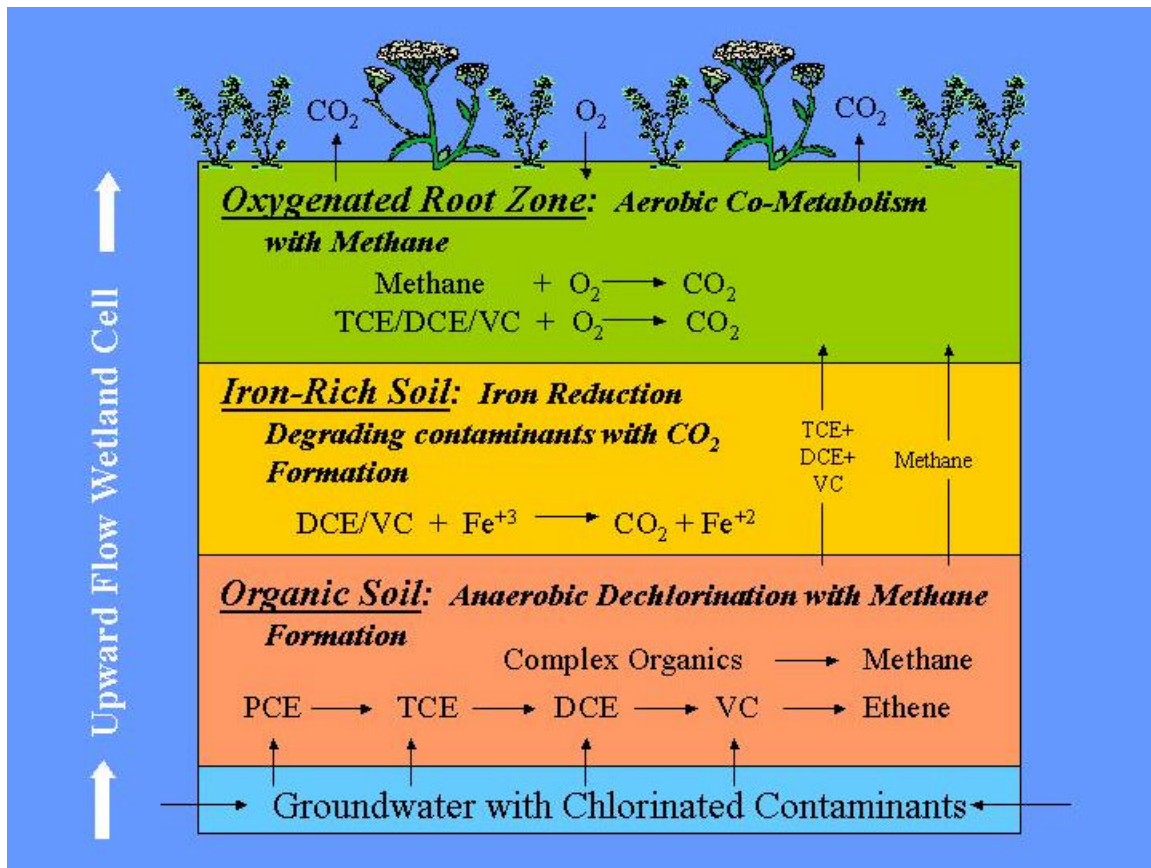
Figure 2. Sequential treatment concept for complete destruction of chlorinated ethenes using upward flow through sediment layers of different characteristics.

In Figure 2, contaminated water is introduced into a gravel layer beneath vertically stratified sediment layers, creating a uniform vertical percolation through sequential reaction zones designed to optimally act on contaminant forms passing from the zone below. The lowest sediment layer (in this case) is created from high organic fill material, typically from soil historically associated with wetlands. Once saturated and anaerobic, this sediment layer provides highly reducing conditions with methane production. The complex organics undergo fermentation, acetogenesis, and methanogenesis while using heavily chlorinated organics such as perchloroethylene (PCE) as more favorable electron acceptors than CO_2 by removal of a chloride. These chlorinated ethenes can be sequentially dechlorinated potentially all the way to ethene, depending on the prevailing microbial consortium. In the case of PCE contamination, dechlorination to trichloroethylene (TCE) is essential in this layer as PCE is not otherwise easily degraded and cannot be aerobically destroyed. The next constructed fill layer is from a more common endemic soil high in iron (Fe^{+++}) content. This offers an environment where the remaining chlorinated organics can be oxidatively destroyed by populations using iron as the electron acceptor. The effectiveness of this process in the sequence is unknown, but it could offer a cheaper initial construction capital cost in the use of more readily available fill material. The top layer consists of the same organic rich soil as in the bottom layer but is permeated with roots from a heterogeneous mix of wetland species.

These roots drive atmospheric oxygen into the saturated soil, creating radial zones of aerobic conditions finely dispersed throughout the layer. Aerobic microbes will easily thrive here, using as their energy source both exudates from the roots and methane percolating up from the methanogenic zone. These populations can fortuitously co-metabolize remaining organics in the water flow from TCE down to ethene. A constructed system optimized for treatment efficiency should have the potential to completely destroy chlorinated ethenes in the water source with little or no energy input beyond the delivery and pressurization of the feed water. Optimization issues involve the nature of supporting soils, the appropriate species domination and diversity, hydrologic conditions, seasonal differences in loading capacity and other optimal design parameters, exact sequence of contaminant breakdown products toward complete destruction, and development of soil, sediment, and plant conditions in response to varying levels of contaminant introduction.

GOALS AND OBJECTIVES

This project explores and develops concepts for engineering design of constructed wetlands as a natural attenuation system and the use of zero-valent metal reductive dechlorination in groundwater circulation wells (GCWs) for pollution control of chlorinated hydrocarbon contaminated groundwater. It leads to demonstration of a new technology approach to groundwater remediation which would save as much as a million dollars per year at a single remediation site and would apply to hundreds of sites nationwide. An on-going Air Force field laboratory capability with strong university ties is also established for a wide variety of applications in environmental management through ecological engineering.

The long term objective is to establish a productive center of study at Wright Patterson AFB (WPAFB) with a continuing line of research from interdisciplinary teams from the Air Force Research Laboratory (AFRL), the Air Force Institute of Technology (AFIT), and Ohio Universities leading to validated methods of engineering natural environmental systems for beneficial use. This is facilitated in the current effort by construction of wetland research cells in the field at WPAFB.

The current project focused on the following specific objectives:

1. A working system dynamics model of contaminant fate and transport in a wetland ecosystem to express the hypothesized mechanisms of contaminant destruction and identify important design parameters;

2. A working groundwater contaminant fate and transport model to design and optimize a metal enhanced GCW system to treat groundwater contaminated with chlorinated hydrocarbons;

3. A field scale, fully contained, wetland system with multiple cells, complete with water distribution systems and sources of contaminated water, constructed to remain viable for years of future research, attracting multiple sources of funding; and

4. A full set of field experiments as well as associated batch and column studies completed and submitted for publication, documenting zero-valent metal reaction kinetics and GCW design criteria, wetland development processes, characterizing reactive zones for contaminant treatment, and suggesting constructed system enhancement to optimize these processes for beneficial and sustainable long term treatment of contaminants.

RESULTS

GCW Reductive Dechlorination Reactors.
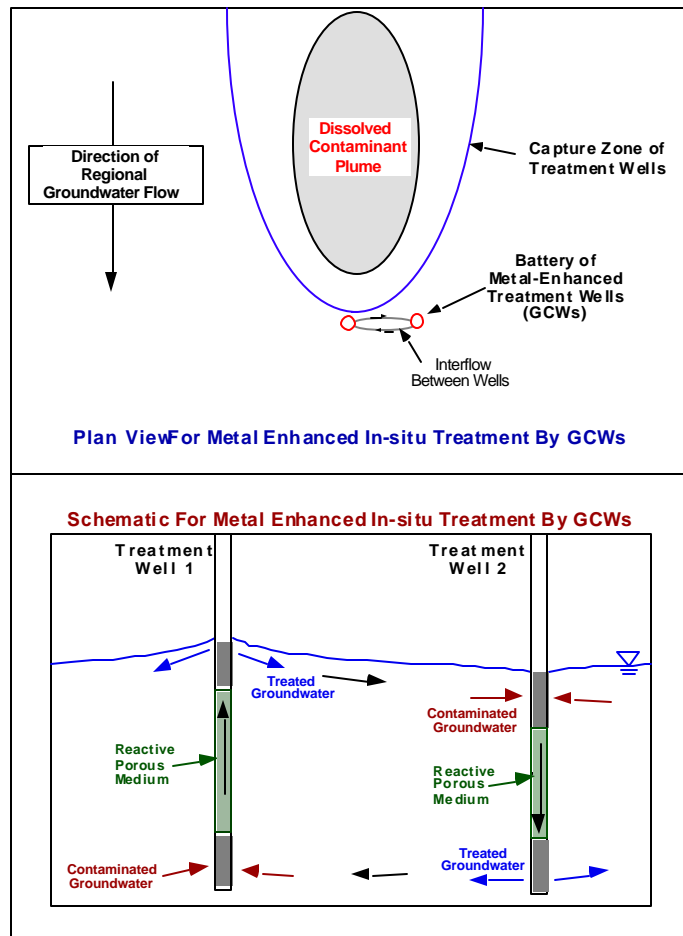
Figure **. Flow schematic for metal enhanced in-situ treatment

A comprehensive literature review was completed of various metal catalysts/reductants that can be used to support the reductive dehalogenation of chlorinated ethenes, indicating that, currently, the most practical catalyst to use in an in-well reactor is palladium (Pd). Existing groundwater circulation well models were modified to incorporate reductive dehalogenation by an in-well Pd catalytic reactor, using first-order degradation rate constants that are typical for Pd catalysts. Modeling results

demonstrated how a circulating well system with in-well palladium reactors might be employed as an innovative technology to contain groundwater plumes contaminated with chlorinated compounds such as PCE and TCE. The model analyses also resulted in figures that could be used by remedial project designers to quickly screen a contaminated site to see if the circulating well system might be an appropriate technology for that site. Results were presented at The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey CA, 22-25 May 00 and published in *The Military Engineer*, 2001.

In conjunction with the laboratory studies conducted at Wright State University, AFIT developed a model of Pd-catalyzed dehalogenation that is more realistic than the simple first-order model initially used. The model simulates Pd-catalyst deactivation by multiple poisons, as well as catalyst regeneration. This model was coupled with simulation of a GCW system. Applying the model under realistic conditions showed that the GCW system could operate approximately 130 days without significant catalyst deactivation. This suggests catalyst deactivation may not significantly affect operating costs or system performance in a real remediation scenario. The model improves our understanding of the processes affecting treatment efficiency and represents an important step in transitioning the technology to field application. Results of this work will be presented at The Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey CA, 20-23 May 02 and published in the *ASCE Journal of Environmental Engineering*. Concurrently, the first-order model was coupled with an evolutionary algorithm, to optimize the design and application of the technology at contaminated sites. A genetic algorithm (GA) was coupled with a three dimensional numerical model of contaminant fate and transport to determine optimized system control parameters (well location, pumping rate, and reactor size). The solution arrived at using this approach, while minimizing cost per unit contaminant mass destroyed, produced unacceptably high downgradient contaminant concentration levels. It was concluded that by specifying only two wells in the GCW system, the problem was over-constrained, and that a multi-well solution is required. Research investigating system optimization is ongoing.

The modeling efforts discussed above will be used to help design a system for field-testing and interpret test results, as well as to prepare guidance for installation of the technology at contaminated sites. With regard to field-testing of the technology, the Department of Defense Environmental Security Technology Certification Program (ESTCP) agreed to fund a two-year field evaluation of the technology. Preliminary work began last year, with site construction scheduled to commence in July 2002 at Edwards AFB in California.

A controlled laboratory approach was completed for studying the reaction kinetics of contaminants in the presence of a catalyzing metal surface. Batch studies have determined contaminant degradation rate constants under varying conditions (initial contaminant concentration, total surface area of palladium available, and varying concentrations of hydrogen [electron donor for the dechlorination reaction], inorganic solutes [such as chloride], and pH). The batch studies demonstrated that degradation of chlorinated ethenes using a Pd catalyst was extremely rapid and that a Pd catalytic reactor

could potentially be used as a component in an in-well flow through system. Degradation products and their further breakdown by the same metal enhanced process have also been studied. Complete degradation of chlorinated ethylenes has been clearly demonstrated without the addition of energy to the process. It was also shown that hydrogen limitation in the Pd reactor might result in the production of two-, three-, and four-carbon byproducts, emphasizing the importance of supplying sufficient hydrogen to the in-well reactor. Batch study results were presented at the 220th meeting of the American Chemical Society in Washington DC in Aug 00 and the Theis Conference 2000, sponsored by National Ground Water Association, in Jackson Hole in Wyoming in September 00. These data provided baseline reaction kinetics information under static conditions in order to move toward investigating the processes under continuous flow in laboratory column studies.

In a series of column studies, WSU evaluated the factors affecting dehalogenation rates for trichloroethylene, perchloroethylene, and three dichloroethylene isomers using supported Pd catalysts with hydrogen gas, studying the effect of flow rate, substrate concentration, catalyst bed configuration, and catalyst deactivation by sulfide and chloride ions, etc. upon dehalogenation kinetics. Degradation products were also measured. The column studies indicated that reaction kinetics transition from Michaelis-Menten type behavior to first-order as the ratio of catalyst to contaminant increases. Results of the column studies will be presented at The Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey CA, 20-23 May 02.

Constructed Vertical Flow Wetlands.

System modeling of a constructed vertical flow wetland was completed which ties together the various processes occurring within wetland sediments and their influence on each other. It is structured to simulate the engineering design of the constructed field cell phase of the work. Results point to the importance of the ability of plants to drive oxygen into the root zone of the soil as well as the importance of optimizing microbial metabolic activity related to contaminant destruction (both reductive dechlorination and oxidative destruction). Model results show that hydrogen (a major product of natural organic matter breakdown) plays the dominant role in both methane production and dechlorination of the contaminants. Certain levels of hydrogen may favor methane production over dechlorination while lower levels of hydrogen may favor dechlorination over methanogenesis. This poses an interesting optimization problem in that dechlorination is the primary objective in the lower region of sediment, but methane production is also desired for flow to and use in the top layer as part of the envisioned sequential degradation of contaminants. These parameters can be controlled by the selection of dominant plant species and the creation of environmental conditions which favor certain microbial populations within the various sediment layers (organic material amendment, inhibition of nitrates and sulfates, for example). The model can explore alternative combinations of engineering actions which lead to improved treatment efficiency. For example, given the slower dechlorination of cis-dichloroethene found in typical wetland soil experiments at Wright State (see below), the potential importance of

an Fe^{+3} layer of soil above such a layer in the field is now evident. It is expected that an Fe^{+3} layer will be able to quickly convert remaining chlorinated ethenes to carbon dioxide and water under the right conditions. Model results indicate that a high level of organic acids (products of natural organic material degradation in the lower soil layer, like hydrogen) strongly competes for the iron and lowers the life of viable iron levels able to destroy chlorinated ethenes. This further complicates the optimization problem. Breakdown of natural organic matter in the lower soil level is necessary for production of hydrogen to drive dechlorination, but this process also produces organic byproducts which then compete for the iron in the next sequential soil layer. Exploring these complex reactions as they simultaneously interact will reveal engineering optimization approaches to improve overall system efficiency. Alternative formulations of the model also explored different concepts of physical orientation of the microbial consortia around the geometry of sediment particles (uniform distribution vs. biofilms, for example).

Biofilm Modeling: A concept not explored in this work (but a subject of planned follow on work) is exploring the accuracy of the assumption (in the modeling formulation) that biodegradation takes place in the aqueous phase of the pore water within the sediment. It is commonly accepted that the bulk of the active microbial biomass is attached to sediment particles, probably in the form of a biofilm.   Conceptually, substrate removal from an aqueous phase requires diffusion of all metabolic reactants into the biofilm, metabolism by the organisms, and diffusion of the metabolic products back through the biofilm and into the aqueous phase (Williamson and McCarty, 1976). This basic rationale has been used extensively over the past 25 years in research involving the removal of aqueous phase substrates by biofilms (Rittmann and McCarty, 1978, 1980, 1981; Suidan and Wang, 1985; Wang, Suidan, and Rittmann, 1986; Saez and Rittmann, 1988; Dykaar and Kitanidis, 1996; Polprasert, Khatiwada, and Bhurtel, 1998; MacDonald et. al., 1999). Figure 3 is the conceptual biofilm model initially considered for this research.
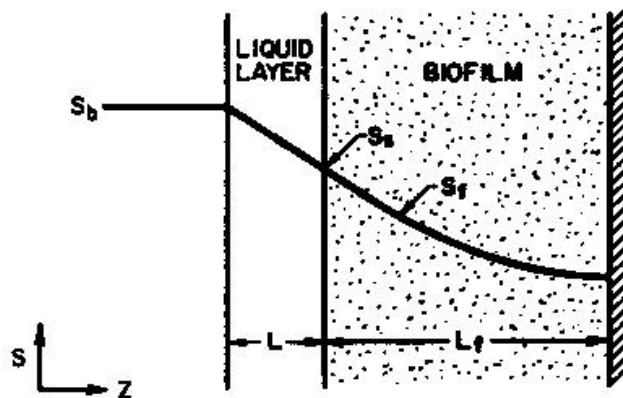
Figure 3. Schematic of Substrate Distribution in a Planar Biofilm (Suidan and Wang, 1985).

The steady state substrate flux though the stagnant liquid layer, L (L), is determined by multiplying the substrate concentration gradient between the bulk liquid phase, S_b (M/L^3), and the biofilm surface, S_s (M/L^3), by the substrate mass-transfer coefficient, k_c (L/T):

$$J_s = k_c (S_b - S_s)$$

where J_s is the substrate flux per unit area of biofilm through the stagnant liquid layer (M$_S$/L^2-T). An important part of the biofilm model is the explicit incorporation of mass-transport resistance from the bulk liquid, through the stagnant liquid layer, and to the biofilm surface (Rittmann and McCarty, 1981). Mass-transport resistance is expressed here by using a mass-transfer coefficient which can be calculated by dividing the molecular diffusion coefficient of the substrate through water by the stagnant liquid layer thickness, L (Rittmann and McCarty, 1978, 1980, 1981; Suidan and Wang, 1985; Wang et. al., 1986; Saez and Rittmann, 1988; MacDonald et. al., 1999); L is defined as the equivalent depth of liquid through which the actual mass transport can be described by molecular diffusion alone (Rittmann and McCarty, 1981).

$$k_c = \frac{D}{L}$$

The following equation is used to estimate the thickness of the stagnant liquid layer for each substrate:

$$L = \frac{D(\text{Re}_m)^{3/4}(Sc)^{2/3}}{5.7v}$$

where D is the molecular diffusion coefficient of the substrate through water (L^2/T); Re is the Reynolds number as defined below (unitless); Sc is the Schmidt number defined below (unitless); and v is the average bulk water velocity (L/T) (MacDonald et. al., 1999). The Reynolds number and Schmidt number are defined as follows:

$$\text{Re}_m = \frac{2r_w d_p v}{(1-n)\mu}$$

$$Sc = \frac{\mu}{Dr_w}$$

where ρ_w is the density of water (M/L^3); d_p is the diameter of the soil particles (L); n is the porosity of the soil (unitless); and μ is the dynamic viscosity of water (M/L-T).

Substrate utilization at any point in the biofilm is assumed to follow a Monod relation (Williamson and McCarty, 1976; Rittmann and McCarty, 1978, 1980, 1981; Suidan and Wang, 1985).

$$\frac{dS_f}{dt} = -\frac{kX_f S_f}{K_s + S_f}$$

Here, S_f is the substrate concentration (M/L^3) at any depth Z in the biofilm; k is the maximum substrate utilization rate (T^{-1}); X_f is the uniform microbial concentration in the biofilm (M/L^3); and K_s is the Monod half-velocity coefficient for the substrate (M/L^3).

The decreasing substrate concentration at the biofilm surface, due to substrate utilization, is the driving force behind mass transfer in the biofilm model. As the substrate concentration in the biofilm decreases, the concentration gradient between the bulk liquid and the biofilm increases, thus creating a condition where more substrate will be transported into the biofilm through molecular diffusion. Additionally, daughter product production (TCE, DCE, VC, and Ethene) is also determined with the Monod relationship using a mass conversion factor, f (unitless), that converts moles of parent compound degraded to moles of daughter product produced.

In their 1978 article entitled "Variable-Order Model of Bacterial-Film Kinetics", Rittmann and McCarty take their analysis one step further and derive an analytical solution that solves for the flux of substrate into a biofilm where it is then degraded via a Monod relationship. Some assumptions that they make for this model is that the biofilm is "deep", meaning that the concentration within the biofilm goes to zero before it reaches the particle surface on which the biofilm is attached. Additionally, they define several dimensionless variables in an effort to reduce the number of independent variables involved in the solution. The following are three of the dimensionless variables used in the final solution

$$S^* = \frac{S}{K_s}$$

$$D_f^* = \frac{D_f}{D}$$

$$L^* = \frac{L}{t}$$

where S^* is the dimensionless substrate concentration; S is the substrate concentration in the bulk liquid phase (M/L^3); D_f^* is the dimensionless biofilm diffusivity; D_f is the biofilm diffusivity (L^2/T); L^* is the dimensionless diffusion-layer depth; and t is the standard depth dimension (L) as defined here (Rittmann and McCarty, 1978).

$$t = \sqrt{\frac{2K_s D_f}{kX_f}}$$

Before the mass flux can be calculated, the following parameters need to be defined:

$$\Lambda = \ln(S^*) - \ln\left(2 + \frac{\ln\left(D_f{}^*\right)}{2.303}\right) - 1.8\ln\left(1 + 2L^* D_f{}^*\right) + 3.53$$

$$q = 0.75 - 0.25\tanh(0.477\Lambda)$$

$$C^* = \frac{2D_f{}^*\left(\sqrt{2} + 2L^* D_f{}^*\right)^{(1-q)}}{1.0 + 0.54\left(1 + 0.0121\ln\left(1 + 2L^*\right)\right)\left(1 - 8.325\left(\ln\frac{q}{0.707}\right)^2\right)}$$

$$\left(\frac{J}{A}\right)^* = C^*(S^*)^q$$

The above equations comprise the variable order model solution in which q is the reaction order (unitless) and C* is the dimensionless reaction coefficient (Rittmann and McCarty, 1978). The actual flux per unit surface area, (J/A) (M/L^2-T), is related to the dimensionless flux per unit surface area, (J/A)*, according to Rittmann and McCarty (1978).

$$\left(\frac{J}{A}\right) = \left(\frac{J}{A}\right)^*\left(\frac{DK_s}{t}\right)$$

With this model, the steady-state contaminant mass-flux into the biofilm can be found for any given contaminant concentration. Additionally, Rittmann and McCarty went on to solve the steady-state contaminant concentration equations for both the complete-mix (CSTR) and the plug-flow reactors. The below equations are the steady-state equations for the complete-mix reactor with the third equation solving for the reaction coefficient:

$$S = S_o - \left(\frac{a}{Q}\right)CS^q \qquad \text{when q} < 1$$

$$S = \frac{S_o}{1 + \dfrac{a}{Q}C} \qquad \text{when q} = 1$$

$$C = \frac{C^* DK_s{}^{(1-q)}}{t}$$

where S_o is the influent concentration (M/L^3); C is the variable-order reaction coefficient for the qth-order reaction; a is the specific surface area (biofilm surface area per unit

reactor volume) (L^{-1}); and Q is the hydraulic loading rate (flow rate per unit reactor volume) (T^{-1}) (Rittmann and McCarty, 1978).

The following equations solve for the steady-state contaminant concentration in a plug-flow reactor using the specific surface area, a (L^{-1}), and the surface loading rate (flow rate per unit cross-sectional area), v (L/T),

$$S = S_o e^{\left(\frac{-Cax}{v}\right)}$$

$$S = \left[(S_o)^{(1-q)} - \frac{Cax(1-q)}{v} \right]^{\frac{1}{1-q}}$$

where S>0 and x is the distance along the reactor (L).

Sample Extraction: Researchers performed tests on two accepted methods for sample extraction: ISCO VOC Sampler and Solinst Peristalic Pump. One procedure and equipment set would be chosen in order to keep consistent sampling procedures in all areas of study and to reduce cost. The peristaltic was abandoned due to the adsorption properties of its flexible silicon tubing and to the potential loss of VOC analytes due to degassing by changing partial pressures in the system (Wilson, 1995). Exchanging check-valves for cap and septums (exposing to air), and the shear weight and awkward configuration in a wetland contributed to the elimination of the ISCO VOC sampler.

A syringe-tube assembly provided minimal sorption and offered fine-tuned control of purge and sampling rates while minimizing time and work surface area in the wetland. The assemblage is shown in Figure 4.

100 mL Syringe

3-way cockstop

1/4" O.D. X 1/8" I.D. Teflon Tubing
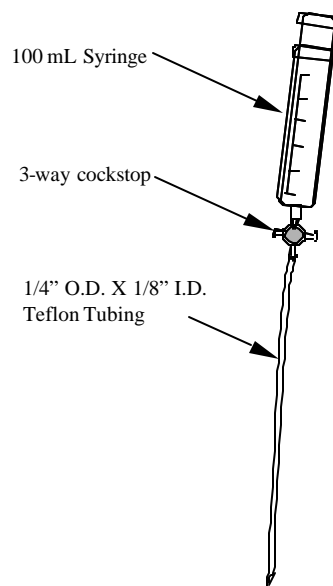
Figure 4. Extraction Assembly

The method called for forcing a ¼" Teflon tubing down the 1/2" Teflon piezometer tubing until breeching the screened area. At the point where the 1/2" Teflon tubing intersects the screened portion a small lip can block passage of the tubing. To penetrate this area the tubing was frayed and cut at an angle. Repeated, forceful movements were sometimes required to penetrate this area. Once in place, the piezometer was purged completely. Samples were then drawn when sufficient water volume was available in the piezometer from recharge from the zone to be sampled. Due to compaction from construction, recent disturbance of piezometer placement and wetland vegetation planting it was not uncommon to see the well recovery rates vary dramatically not only from strata to strata, but across the surface area of the cell. Recovery rates were taken at all sampling points to establish a purging procedure in order to obtain a water sample that is from the soil matrix in a "timely" manner.

Biotic and abiotic processes effecting stagnant water could bias analytical results that are not indicative to the adjacent water matrix. MacGowan and Surdam (1994) found a 15% reduction in acetate concentrations from a 1220-hour stagnant solution. Errors introduced through improper purging of stagnant water were found to be greater than errors associated with sampling mechanisms, tubing, and construction materials (Wilson, 1995).

Piezometer Water Recovery: Due to compaction from construction, recent disturbance of piezometer placement and wetland vegetation planting it was not uncommon to see the well recovery rates vary dramatically not only from strata to strata, but across the surface area of the cell. Recovery rates were taken at all sampling points to establish a purging procedure in order to obtain a water sample that is from the soil matrix in a "timely" manner.

The bottom strata displayed no problems with recovery and could be purged and sampled during the same procedure. After observing and recording the recovery of sampling points in the top 2 strata, it was determined that those piezometers that could not meet a recovery rate of 3.0mL/hr would be developed by surge pumping and purging using existing wetland surface water. This method of development included purging the piezometer, then immediately surging with a peristaltic pump. The process was repeated three times from each piezometer selected for development. 3.0mL/hr was chosen as the benchmark to allow discarding the first 20mL during extraction and a sampling volume of 50mL in the syringe before transferring into 40mL vial following a complete purge twenty-four hours prior. Ten piezometers in the middle stratum and twenty-six in the top stratum initially fell below the 3.0mL/min standard. After development only two piezometers could not meet the recovery rate standard.

A purging-to-sampling elapsed time of twenty-four hours was initially chosen to ensure consistency among study areas. After development, the rates improved so much that a "timely" purge to sample recovery time shrunk to approximately two hours (vs. twenty-four).

Sampling Procedure: The sampling tubing was placed back into the piezometer following the purging of all piezometers in a particular strata. The first 20mL in the

syringe was discarded by turning the cockstop so as to keep a vacuum in the line while at the same time ridding the syringe of first 20mL. This step is part of the procedure for two reasons: 1) it primes the line to keep air from reaching the sample and 2) in between samples the line and syringe are flushed with DI water, this step keeps the sample from being diluted with residual DI water in the assembly. After discarding, approximately 50mL is pulled into the jumbo syringe. At which time the cockstop is again turned to allow 40mL+ to fill a 40mL vial. As the strata was sampled, all filled vials were maintained in an ice bath cooler before transporting to the laboratory for sample preparation so as to minimize any biodegradation or other abiotic processes in the sampling vials.

Sample Preparation: Once the samples were retrieved from cell #1, they were taken immediately to the laboratory at AFIT for preparation. Once at the lab, 5mL were drawn from the 40mL vial and then filtered using a 0.45 µm syringe Teflon membrane filter into a Dionex disposable 10mL autosampler vial. A head space was required for the autosampler vial per manufacturer instructions. Filtering reduces interference among other organic compounds. Water soluble organic compounds can sometimes co-elute with organic acids and yield system peaks that interfere with organic acid detection (Chen, 1996). If the samples could not be analyzed within twenty-four hours from extraction, the samples were maintained in an ice water bath until being analyzed, but not to exceed one week from extraction. A laboratory study showed these acids disappeared using a nonsterile organic-rich sample in 28 days (Kramer, 1990).

GC methodology for volatile organics: Standard solutions and wetland water samples were analyzed for chlorinated organics by purge and trap gas chromatography. The specific methods were adapted EPA Methods 5030 and 8260B. The 40 mL VOA sample vials containing either standard solutions or actual wetland samples were placed in an Archon AutoSampler system built by Varian Analytical Instruments. The Archon AutoSampler was used in concert with an Encon Purge and Trap sample concentrator. Specific operating parameters of the instrument are shown below.

Sample Volume (mL)	5
Purge Gas	Helium
Purge Gas flow Rate (ml/min)	40
Purge time (min)	11
Purge Temp (deg C)	Ambient
Dry Purge time (min)	2
Desorb preheat (deg C)	245
Desorb Temp (deg C)	250
Desorb time (min)	2
Bake time (min)	10
Bake temp (deg C)	250
Moisture Reduction Bake (deg C)	260 (used to remove moisture from the trap after run)

After the sample is desorbed from the Encon Purge and Trap it is sent to the GC. The GC used in this effort was set up using a split column configuration. In this configuration, a splitter was used to send the sample into two columns and two detectors after injection

into a single inlet. The front column was a Restek RTX-VRX and was connected to the micro-Electron Capture Detector (µECD). The back column was a J&W 113-4332 GS-GASPRO and was connected to the flame ionization detector (FID). GC program parameters were:

Oven

Initial Temp (deg C)	50
Initial Time (min)	1.50
Ramp (deg C/min)	10.00
Final Temp (deg C)	220
Hold Time at final Temp (min)	0
Post Temp (deg C)	50
Total Run Time (min)	18.50

Front Inlet   **Back Inlet (not used)**

Mode:	Split
Initial Temp (deg C)	200
Pressure (psi)	15.00
Split Ratio:	5:1
Split Flow (mL/min)	20.6
Total Flow (mL/min)	27.8
Gas Saver:	On
Saver Flow (mL/min)	20.0
Saver Time (min)	2.00
Gas Type:	Helium

Column 1 (Restek RTX-VRX)

Max Temp (deg C)	260
Nominal Length (m)	20
Nominal Diameter (µm)	180
Nominal Film Thickness (µm)	1.00

Mode	**Const Press**
Pressure (psi)	15.00
Nominal Init Flow (mL/min)	0.5
Average Velocity (cm/sec)	24
Inlet	Front
Outlet	Front
Outlet Pressure	Amb

Front Detector (µECD)

Temp (deg C)	250
Mode:	Constant Column+makeup flow
Combined Flow (mL/min)	45
Makeup Flow:	On
Makeup Gas Type:	Nitrogen
Electrometer:	On

Column 2 (J&W 113-4332 GS-GASPRO)

Max Temp (deg C)	260
Nominal Length (m)	30
Nominal Diameter (µm)	320
Nominal Film Thickness (µm)	n/a

Mode	**Const Press**
Pressure (psi)	15.00
Nominal Init Flow (mL/min)	3.6
Average Velocity (cm/sec)	52
Inlet	Front
Outlet	Back
Outlet Pressure	Amb

Back Detector (FID)

Temp	250
Hydrogen Flow (ml/min)	40.0
Air Flow (mL/min)	400.0
Mode: Const Column+Makeup Flow	
Combined Flow (mL/min)	20.0
Makeup Flow:	On
Makeup Gas Type:	Nitrogen
Flame:	On
Electrometer:	On
Lit Offset:	2.0

Role of organic acids: While decomposing vegetation is a source of carbon for a lot of microorganisms in wetland soils, organic acids both function as by-products and substrates in the ecosystem. These acids can serve the casual observer as an indicator of biomass activity. Organic acids, especially acetate, are important products and substrates for diverse microbial processes, especially in anaerobic habitats (Seagren and Becker, 1999). In anaerobic environments, complex organic compounds can only be mineralized through the concerted activities of multiple, inter-dependent populations (Seagren and Becker, 1999). Thus, in these systems, continuous removal of reaction products by syntrophic populations is necessary in order to sustain the oxidation of complex organic compounds (Seagren and Becker, 1999).

Two of the major anaerobic processes are fermentation and methanogenesis. The fermentation of organic matter, also called glycolysis for the substrate involved, occurs when organic matter itself is the terminal electron acceptor in anaerobic respiration by microorganisms and forms various low-molecular weight acids and alcohols and CO_2. Examples are lactic acid shown below.

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OCOOH \text{ (lactic acid)}$$
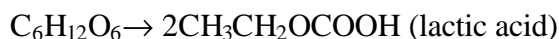
Not only will organic acids like lactic and acetic give rise to the bioremediation efforts in different zones of the wetland, they can also classify the reducing traits of that zone. Acetate concentration measurements in sediments in which CO_2, sulfate, or Fe(III)-reduction were the predominant terminal electron accepting processes (Lovely and Phillips, 1986) suggest that a similar relationship may exist between the thermodynamics of the electron acceptor half-reactions and acetate concentrations in anaerobic environments (Seagren and Becker, 1999). One objective of this study is to determine an anion profile within the constructed wetland one year after initial operation and relate that profile to microbial-mediated degradation of the chlorinated ethenes.

Some unique bacteria have the ability to reduce highly chlorinated ethenes such as PCE. Frequently, PCE and TCE persist for years without change, because electron donors required for halorespiration are absent (McCarty, 1997b). Some PCE-dechlorinating organisms appear versatile at using electron donors and acceptors, while others, most notably *"Dehalobacter restrictus," "D. ethenogenes,"* and strain TT4B apparently can only use a single electron donor and only chlorinated aliphatic hydrocarbons as electron acceptors (Gosset and Zinder, 1997). Species such as these can work symbiotically in wetland environments where competition for electron donors is healthy. In cases where organic materials are present to provide the electron donors required for halorespiration, the complete destruction of PCE and TCE under anaerobic conditions involves consortia of many microorganisms working together (McCarty, 1997b).

<u>Organic Analytes</u>: Low-molecular weight, mono-carboxylic organic acids play vital role in the pathways at which degradation is possible. Methanogenic bacteria can conveniently supply these necessary low-molecular-weight organic compounds such as lactate and ethanol for sulfur-reducing bacteria (Mitsch and Gosselink, 2000):

$$2CH_3CHOHCOO^- \text{ (lactate)} + SO_4^- + 3H^+ \rightarrow 2CH_3COO^- + 2CO_2 + 2H_2O + HS^-$$
$$\text{and}$$
$$CH_3COO^- \text{ (acetate)} + SO_4^- \rightarrow 2CO_2 + 2H_2O + HS^-$$
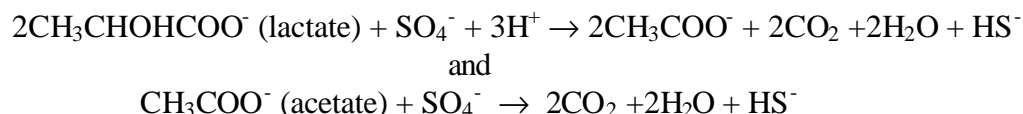
Some see organic acids as the tool necessary to predict bioremediation. Knowing the distribution of microbially-mediated redox processes is key to predicting the fate and transport of organic and inorganic contaminants in groundwater systems (Seagren and Becker, 1999).

The organic anion analytes of interest in this study are propionate, butyrate, lactate, acetate, and formate. Previous research of organic acids have shown both lactate and acetate to dominate the total acid concentrations in a wetland. Unusual signs of others may be correlated to further research and provide a valuable monitoring and predicting tool. Cizkova et. al (1999) found acetic and lactic acids in various wetlands at greater than 50% of the total mono-carboxylic acid concentrations detected.

Fermentation of humic substances and organic acids is expected in the anaerobic strata that will enchance the reductive conditions necessary for the biodegradation pathways shown above. Fermentation of butyrate and propionate can lead to metabolites of acetate, hydrogen, and bicarbonate, which serve as precursors to methanogensis (Van Lier, 1993). General agreement exists that anaerobic conditions that support methanogensis are needed to reduce PCE. Freedman and Gossett (1989) found that PCE reduction to ethane was possible given significant attenuation under methanogenic conditions. Mono-carboxylic acids lay the foundation for reductive environment. Their ubiquitous nature in wetlands and integral component to the processes conducive to bioremediation suggest the need for this research.
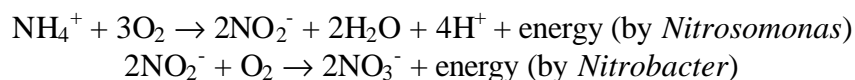
<u>Inorganic Analytes</u>:   Concentrations of chloride, fluoride, nitrate, nitrite, and sulfate can provide valuable insight to the ecology of the cell. Some of these analytes are expected naturally to some degree in both the wetland and in the aquifer that feeds cell #1. However, the trends that each take as they progress through the wetland are of particular interest.

Chloride concentrations have been used as a tracer to quantify mass transfer processes and an estimator of evaporation in wetlands (Hayashi, 1998). Chloride's conservative nature in most terrestrial environments and use in the contaminants make it an analyte of interest. Nitrates and sulfates are commonly used electron acceptors for many cultures of anaerobic microorganisms.

Their changes in concentrations paint a picture of the metabolic reactions and reductive conditions that exist throughout the wetland. Constructed wetlands are effectively used for nitrate removal. Wetlands have two environmental characteristics that promote dentrification: (1) the sediments are anoxic, a requisite condition for denitrification, and (2) plant growth provides a source of carbon fuel (Ingersoll and Baker, 1998). Inorganics such as nitrates and sulfates have a correlation to the organic acid amounts seen in wetlands. Cozzarelli and others(1994) state that low-molecular-weight organic acid concentrations are controlled, in part, by the presence of electron acceptors available for microbially mediated electron transfer reactions. Cozzarelli adds that the depletion of electron acceptors leads to accumulation of aliphatic organic acids in anoxic groundwater.

Nitrite concentrations can give indications on the nitrification and denitrification processes prevalent in the wetland. Mitsch and Gosselink (2000) demonstrate the nitrification of ammonium by *Nitrosomonas* and *Nitrobacter* where the ammonium is transferred to nitrate:

$$NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{energy (by } Nitrosomonas\text{)}$$
$$2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy (by } Nitrobacter\text{)}$$

Nitrification can also occur in the oxidized rhizosphere of plants where adequate oxygen is often available to convert the ammonium nitrogen to nitrate nitrogen (Reddy and Graetz, 1988).

IC Anion Analysis Method: Recent literature has proposed the use of ion exchange chromatography as the instrument of choice for organic acid qualitative and quantitative measurements. Ion exchange chromatography has proven to be more efficient and sensitive versus ion exclusion. A Dionex Ion Chromatograph (IC) system was chosen for the analytical portion of this study. The Dionex 600 series IC system consisted of an EG40 Potassium Hydroxide Eluent Generator, GP50 Gradient Pump, AS50 Autosampler, CD25 Conductivity Dectector, 4mm self-regenerating Ultra Supressor (used in recycling mode), and thermal compartment housing an AG-11 guard column and AS-11HC separating column. As shown in Figure 5, the gradient pump pushes De-Ionized (DI) water and eluent at concentration levels set by the program into an injection port. At the injection port, a loop is loaded with a 10µL wetland sample where it then passes through a guard column. The guard column protects the separation column from particulates that could permanently damage it and allows more effective separation of peaks. Once the sample is in the high capacity separation column, the hydroxide ion comes into competition with the analyte anion as it partitions from the mobile to stationary phase and then back to the mobile phase, thus allowing the different analytes to separate before entering the suppressor. The competition role that the eluent plays allows analytes that would normally take longer to be seen in the detector to push through the column and on to the detector much sooner due to the analyte's partitioning coefficient once in the column and/or relative molecular size. Once in the suppressor, the analyte and eluent pass through cation exchange membranes where the K^+ ion passes through to form KOH and H_2 from DI water in contact with a cathode. At the same time, H^+ ions are passing

through another cation exhange membrane to form H_2O with the hydroxide ion in the eluent, thus leaving only analyte and water to the conductivity detector allowing a lower baseline and detection limit.
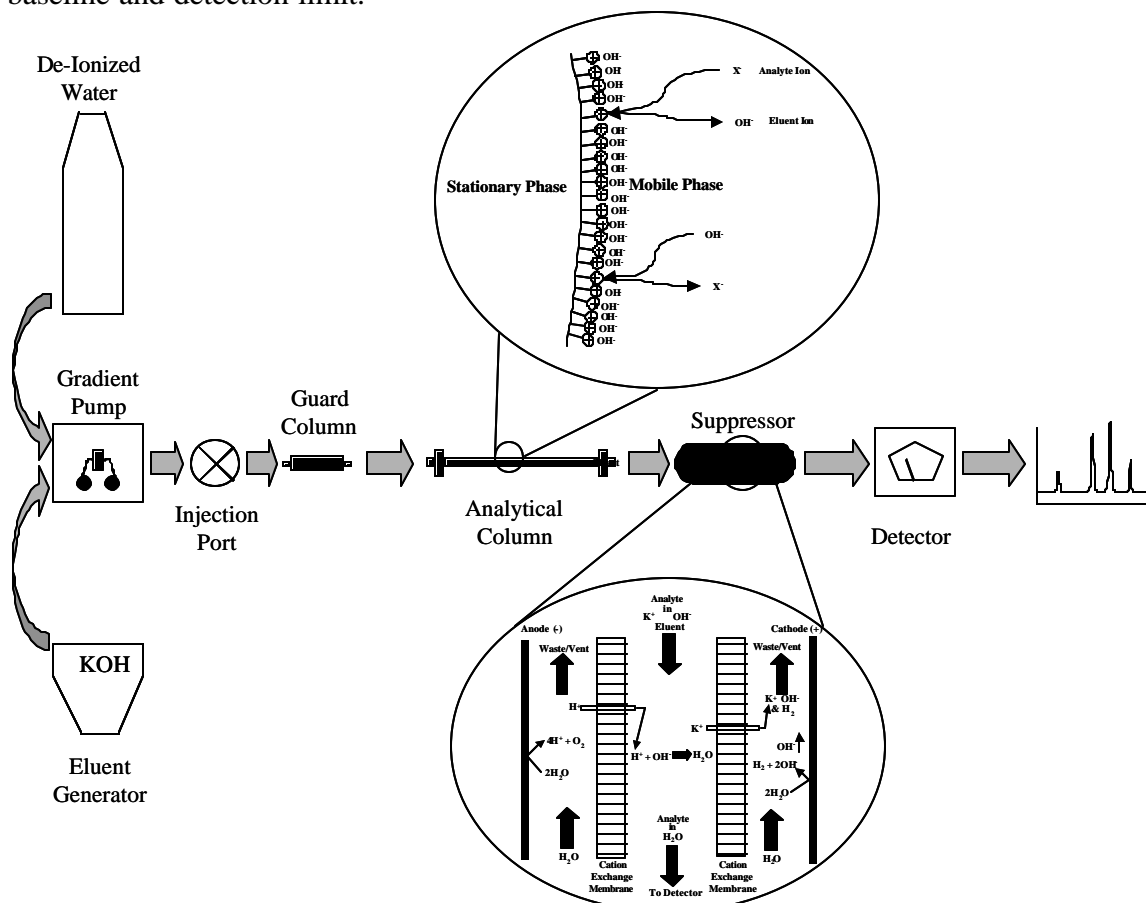
Figure 5. Ion Chromatography Flow Diagram

After several qualitative trials, a method was developed that varied the eluent concentration at a flow rate of 1.50mL/min in order to get identifiable separation of peaks among the mono-carboxylic acids. The method calls for 10μL of sample to be injected with 1mM of KOH eluent at time 0.0 minutes. The eluent concentration then ramps from 1 to 8mM of KOH after 8.0 minutes and again from 8 to 30mM of KOH from 8.0 to 28.0 minutes. The last ramp of KOH concentration happens from 28.0 to 38.0 minutes with values of 30 to 60mM respectively. After 38.1 minutes the KOH concentration reduces to 1mM until the 41.5 minute mark for the system to re-equilibrate. While sulfate proved to be the last analyte at 23.550 minutes, high KOH concentrations produce undesirable conditions in the column for any residual analytes and are a critical portion of the analysis procedure. A blank sample is run prior to each batch of prepared samples. Table 1 shows the program used by the Dionex PeakNet 6.30 software to control the major components and parameters of those components during analysis.

An injection loop of 100μL allows calibrations to be performed by increasing injection volumes of standards prepared in the laboratory. Dionex PeakNet 6.30 software constructs calibration curves based upon developed external standards and can apply

these curves to a sequence of samples giving identification and concentrations upon sequence completion. Detection parameters must be prior adjusted to assure confidence in the calibrated results.

Table 1: Dionex Analysis Program for PeakNet 6.0

	Pressure.LowerLimit =	200
	Pressure.UpperLimit =	2500
	%A. Equate =	"Water"
	%B. Equate =	"%B"
	%C. Equate =	"%C"
	%D. Equate =	"%D"
	Flush	Volume = 100
	Wait	FlushState
	NeedleHeight =	5
	CutSegmentVolume =	10
	SyringeSpeed =	3
	ColumnTemperature =	30
	Cycle =	0
	Data_Collection_Rate =	2.0
	Temperature_Compensation =	1.7
	Oven_Temperature =	30
	Suppressor_Type =	SRS
	Suppressor_Current =	100
	Flow =	1.50
	%B =	0.0
	%C =	0.0
	%D =	0.0
	Pump.Curve =	5
	WaitForTemperature =	False
	Wait	SamplePrep
- 0.100	; this negative step is for command traffic	
	Concentration =	1.00
	EluentGenerator.Curve =	5
0.000	ECD.Autozero	
	Load	
	Wait	CycleTimeState
	Inject	
	Wait	InjectState
	ECD_1.AcqOn	
	Concentration =	1.00
	EluentGenerator.Curve =	5
8.000	Concentration =	1.000
	EluentGenerator.Curve =	5
28.000	Concentration =	30.000
	EluentGenerator.Curve =	5
38.000	Concentration =	60.000
	EluentGenerator.Curve =	5
38.000	ECD_1.AcqOff	

	Concentration =	60.000
	EluentGenerator.Curve =	5
38.100	Concentration =	1.000
	EluentGenerator.Curve =	5
41.500	Concentration =	1.000
	EluentGenerator.Curve =	5
	Wait	
	End	

Laboratory flask, small column, and greenhouse experiments were conducted to test the methane generation potential of various soils collected from historical natural wetland areas. Microcosm bench studies have defined field conditions which will optimize methane generation. These hydric soils were mixed with woody yard waste, leaves, grass clippings, and straw as potential amendments to the soil for methane generation. Experimental data has quantified the ratios of hydric soil and composted organic material that produce varying amounts of methane in controlled conditions. Straw seems to have the most rapid fermentation and produces visible gas. The potential for generating methane is a critical aspect of efficient treatment of contaminants within the hypothesis presented here for treatment optimization in the field scale constructed wetland cells. Additional experiments using pre-prepared anaerobic microorganism seed material have demonstrated the importance of seeding lower layers of the constructed wetland to achieve quick contaminant treatment conditions in the field. These results guided the final construction phase of the field demonstration (see below). Separate plant species studies were conducted to determine differential ability to foster methane oxidation within the root zone just below the surface (consistent with the engineering design concept) (Fig 2). Plants differentially force oxygen into the soil and provide conditions for aerobic microbial populations to oxidize methane as a primary food source (and low levels of contaminants as a secondary food source). Data have shown no statistical difference among the species tested in ability to oxidize methane in aerobic conditions or produce methane in anaerobic conditions when the roots are extracted from the soil and studied separately in solution. Experiments have also confirmed that anaerobic populations are not threatened during brief oxygen exposure that would be expected during construction phases.

Bench level microcosm soil studies evaluated the potential of naturally occurring microorganisms in the destruction of perchloroethylene and its degradation products. Soil from a drained wetland was used in microcosms to assess the ability of a naturally occurring microbial consortium, having no previous exposure to chlorinated ethylenes, to reductively dechlorinate perchloroethylene to a harmless end product. The sequence of degradation products leading to harmless by-products (ethene) by reductive dechlorination is depicted in Figure 6. Long term studies (6 months) revealed PCE dechlorination, in the presence of abundant methanogenesis, with cis-DCE as the major transformation product. Dechlorination of cis-DCE was shown to increase when PCE was no longer detectable. Adding additional easily degraded organic material (yeast

extract) to provide optimal hydrogen conditions failed to improve dechlorination beyond DCE. These results confirm that additional oxidative destruction of DCE may be important in layers above a highly reducing sediment layer. High H_2 production resulted in methanogenesis and reductive dechlorination occurring simultaneously. The disappearance time of a fixed amount of PCE decreased from 35 days to 5 days over a period of 90 days. PCE dechlorination resulted in rapid accumulation of cis-DCE and sluggish production of minor amounts of vinyl chloride and ethene. This suggests that the indigenous microbes are capable of PCE dehalogenation to ethene, although complete dechlorination is relatively slow. Supernatant fluid from two microcosms was used to make four soil-free microcosms to determine the feasibility of transferring dechlorinating microbes and maintaining an active dechlorinating microbial community. Albeit quite slow, these systems are active as indicated by H_2 consumption, biomass accumulation, methane production at significant H_2 concentrations, and evidence for PCE dechlorination as TCE production.
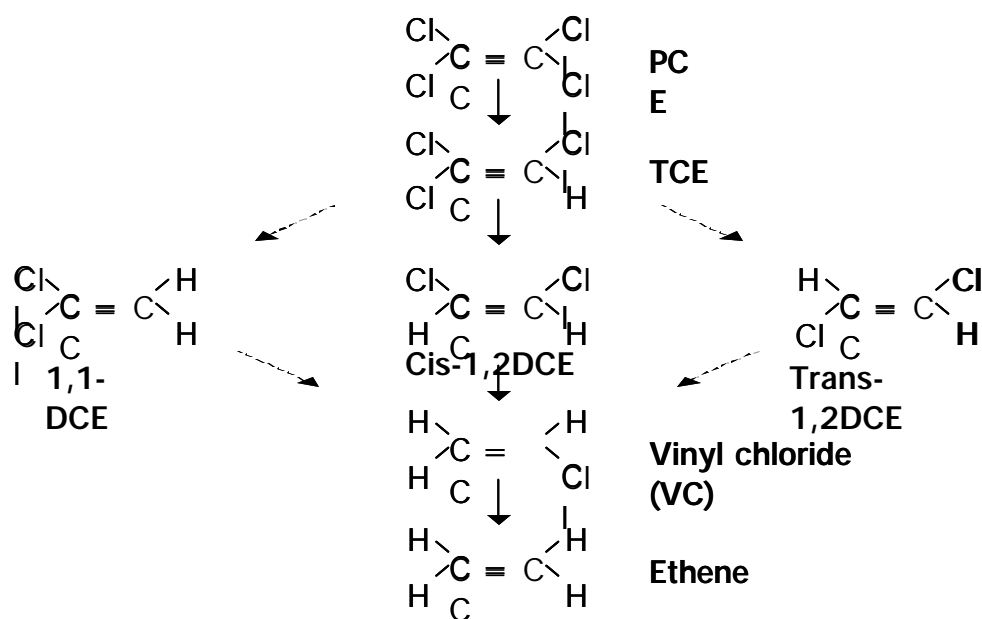
Figure 6. Sequential breakdown products of reductive dechlorination of PCE.

Figure 7. Methane generation and oxidation studies with plant species at Wright State University.

Laboratory column studies performed at Wright State suggest that sufficient methane generation exists in all practical field conditions with only slight (insignificant) differences in methane production and oxidation among different wetland plant species. Follow-on column studies, using trichloroethene (TCE) as a contaminant, demonstrate a hundred fold decrease in TCE from the bottom to the top of the upward flow column. No intermediate degradation products have been detected, suggesting that TCE (and intermediate products) is either completely oxidized to carbon dioxide or bound within the soil matrix of the column. Strong binding within the soil is consistent with expectations and is considered a favorable phenomenon for optimization of treatment in the field. Data also suggest that significant degradation is occurring in addition to binding.

Additional column studies simulated the conditions of the top soil layer of the field demonstration cells permeated with rooted plants. Roots developed in the columns as deep as 5 feet, suggesting that a 5 foot upper rooted soil layer can be used to extend contact time with flowing contaminants (Fig 8). Using a typical wetland plant species (Carex hystericina) the soil was characterized by a dense concentration of roots creating a finely heterogenous mix of both aerobic and anaerobic regions. Root surface area in Carex hystericina raised in upward flow conditions represents a large area for potential TCE uptake. Root hairs (0.0008 cm in diameter) made up a significant amount of the observed surface area and could be important sites for nutrient uptake and TCE transport. Mesocosm studies suggest that roots in a treatment cell with up-flowing water will penetrate about three times deeper than those grown in surface fed wetlands. Robust root systems exceeded 50 cm in depth in up-flow systems. With the high organic content of the soil (continuously replenished by senescing roots), the anaerobic zones can produce

methane which can then potentiate destruction of contaminants within the aerobic zones. Results suggest that contaminant destruction within laboratory columns present detection limitation problems and that strong methane concentrations may inhibit contaminant destruction even though methane is required at some optimum level to activate the process. This, again, suggests an additional systemic approach for optimizing the entire constructed wetland system, perhaps allowing less dependence on the production of methane in lower soil layers. In addition, should roots be able to penetrate into a lower iron-rich zone within the constructed wetland design, the resulting introduction of oxygen within that zone could allow replenishing of oxidized iron, allowing a recycling effect for continued destruction of contaminants by iron oxidation, extending the life of that soil layer in contaminant treatment. The root zone column studies also demonstrated as much as 50% evapotranspiration (50% of the water flow transported to the atmosphere through the plant leaves) at the flow rates used. This opens the question of how much contaminant may be entering the plants with this evapotranspiration flow. This phenomenon would effectively remove the contaminants from the water flow and would either destroy the contaminant by natural plant metabolic processes or transfer the contaminant to the atmosphere along with the water. Given the apparent strength of this process, a strong line of research is indicted to explore this phytoremediation effect in both natural and constructed wetlands. Continued column studies in this project determined the partitioning of treated contaminant among anaerobic reductive dechlorination, aerobic oxidative destruction, removal from the water by binding to soil, and phytoremediation processes. C-14 labeled contaminants were used to trace their fate within the column. In two separate experiments, varying in duration from one to ten days, a significant amount of ^{14}C-labeled TCE was observed in the leaf tissues of Carex hystericina fed with labeled TCE in the root zone. In addition, ^{14}C-labeled TCE was also detected in the atmosphere surrounding the C. hystericina plant. A plexiglass housing was used to enclose the atmosphere around the column to test for the appearance of airborne contaminants as well as their ultimate degradation product, carbon dioxide. Evapotranspiration (ET) is a significant source of water transport and correlates well with number of leaves and leaf surface area in Carex hystericina. This may provide an easy way to estimate ET in the field in Carex hystericina. Estimates of ET are critical for developing accurate water budgets and estimating residence time in the constructed wetlands. In addition, TCE may be co-transported with water in the plants.

Figure 8. Root development in upward flow columns using Carex hystericina.

Additional columns twice the length of those previously used were developed and provided a doubling of retention time. Retention times which were too short for full treatment were identified as a problem in the previous column work. Plant driven evapotranspiration obviated a minmum input rate of the ground water and the volume of the first columns gave us retention times that produced only minimal microbial degradation. The longer columns were run at the same flow rate as the previous set and clones of the same plants were used to establish the vegetation in the columns. The columns were planted in a mixture of wetland (hydric) soil from the same location that supplies the field constructed wetlands. One part Canada peat was added to about 3 parts of the hydric soil to soften the mixture and allow for good flow of the water. Soils were added to the columns with the water flowing in at about 50 ml per hour to prevent packing of the soil and the plants were added under continuing flow. The flow was then lowered to about 2 ml per hour to mimic previous experiments. The columns were sampled at 5 locations: inlet, three equally spaced samples between the top and bottom of the column, and at the outlet. The plants were grown under 13 hours of light daily (natural supplemented by fluorescent lights) to prevent dormancy in the winter months. On March 15th the day cycle was changed to 18 hours to induce summer-like growth. To sample TCE (or PCE), the gas chromatograph method used Solid Phase Micro Extraction (SPME) onto fibers (in hopes of using very small samples) and has demonstrated detection of TCE to 1ppb and PCE at 50ppt. These fibers will allow the detection of

trace amounts of chlorinated ethenes within the various media of the constructed treatment wetlands. Small sample sizes were essential to enable column sampling without major influences on column dynamics. In addition, the SPME fibers should enable development of a method for sampling the air around the leaves of the plants. Previous results show that a significant amount of TCE was vented to the atmosphere by the plant during its growth and this method will potentially make it easier to describe and quantify that venting.

In the column studies overall, we have discovered that the wetland plant *Carex hystericina* is
1. tolerant of TCE at over 500 ppb
2. capable of venting TCE through its roots to its leaves
3. a robust produces of roots for the uptake and distribution of TCE
4. able to grow better in the presence of TCE than in the controls without TCE
5. appears to have metabolized a small amount of TCE and that product is retained in its leaves
6. a good candidate for the treatment wetland since it is cold hardy and remains active through much of the winter season if illuminated by supplemental light

In addition, column studies designed to investigate methane oxidation and TCE degradation found the following:
1. Some oxidation of methane occurs in the root zone of the plants chosen for the experiment, suggesting that TCE cometabolism is likely.
2. Detection of TCE degradation by cometabolism processes is difficult and irregular, suggesting that intact systems are required for evaluation.
3. TCE is removed from experimental systems by the plants. Venting to the atmosphere is apparently responsible for about 45% of the removal, and about 4% of the TCE may be metabolized by the plants or plant associated microbes. Close to 40% of the input TCE was found in soil, but only 3% of the input was found in water that could be drained from the test column. The remaining TCE was scattered in plumbing and only 0.3% was unaccounted for. The initial TCE concentration in these experiments was about 500 ppb.

Figure 9 presents the TCE mass balance from labeled TCE column experiments.
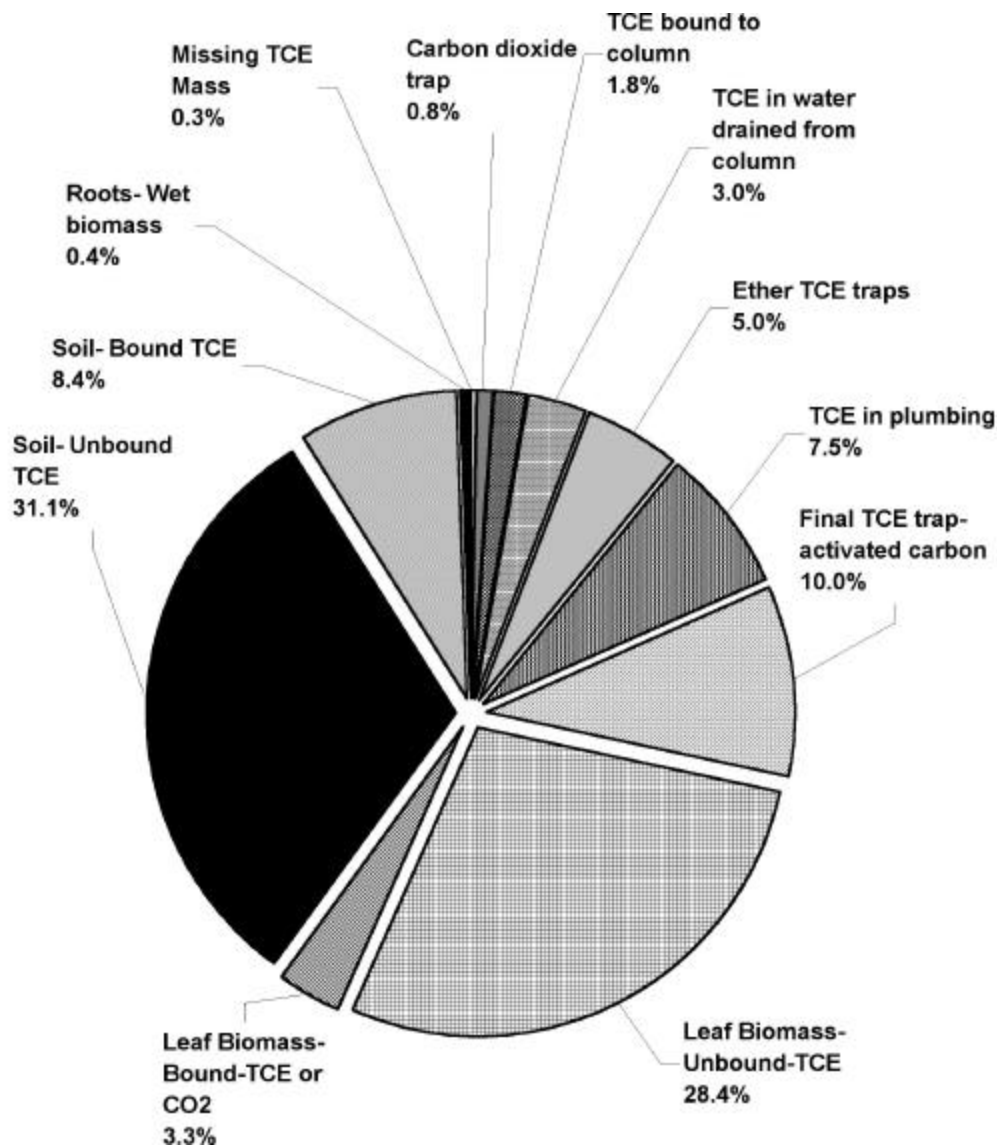
Figure 9. Mass balance of TCE in laboratory plant column flow-through studies.

In addition to bench level studies, a large experimental column was constructed (with supporting platform, experimental sampling ports, and connecting plumbing) and installed at the WPAFB contaminant treatment plant adjacent to Landfill 5. The column was filled with a uniform typical wetland soil and saturated with running water (upward flow) from a TCE contaminated groundwater source feeding into an air stripping treatment plant. Expanded volume of the packed column when pressurized (sufficient to produce an outflow at the top) suggested that fluidization of such soils in a constructed wetland under vertical flow conditions could present a challenge. The column also suggested a significant role for evapotranspiration, producing only 50% of the inflow as actual water overflow at the top when grasses were planted atop the soil column. No TCE from the inflow was detected in the overflow during the 3 month column test under these conditions (Fig 10).

Figure 10. Soil column studies at influent to TCE air stripping plant at WPAFB.

A root/soil coring device was developed that allows visualization of roots at various depths in the soil column. Two cores of natural wetland sites have been completed and have shown that roots of the wetland plants penetrate at least 1.2 meters below the surface. The roots form a dense mat in the zone 0 to 25 cm below the surface and finer and less dense root masses can penetrate through silt and clay. Much of the penetration through clay involves following channels previously made by invertebrates such as crayfish. These channels fill with peat and make a highly organic conduit for the roots. In some locations where the upward flow of water is restricted the roots seem not to penetrate deeply. Although it was not possible to successfully core the coarse sand and gravel below the peat at these sites, observation of the first 5 cm of gravel indicated that roots continued downward. The interpretation of this finding is that the constructed wetland treatment cell should develop similar penetration of roots if it functions as planned.

The construction of the field scale wetland research facility was met with several challenges in siting approval on Wright Patterson AFB (not unexpected). Paramount was the concern over bird strike associated with attraction of fowl to "wetland" areas. The facility was designed to ensure no such attraction would exist (no open water), and the completed facility has demonstrated no attraction of avian species and is continuing to be monitored. The original siting was disqualified because it was directly in line with the south end of the runway within 500 feet of the glide path. Other community "zoning" concerns impacted other alternative locations on the base. The final approved site is adjacent to Skeel Avenue in Area C of the base near Base Operations. A $240K contract was awarded to Brown and Root through the Corps of Engineers for construction at that site. The final construction cost was approximately $320K. This includes two complete wetland cells (140x60 feet each), fully contained and discharging to the Fairborn OH

sanitary sewer system under Ohio EPA Permit to Install # 05-10719. Ohio EPA has had a team on site to study the design concept for future remediation efforts. Construction broke ground in Nov 99 and was completed in Jan 00 ready for Spring planting. Seed was sown in a greenhouse environment in December sufficient to cover one cell of the wetland facility with 10 different wetland species. Twenty different species of wetland plants underwent germination and survival rate studies in greenhouse conditions. Favored plants (using criteria of hardiness, acclimation to groundwater fed wetlands, year-round productivity, survival, and methane oxidation potential) were germinated in sufficient quantity to transplant to the field site. The greenhouse was modified to produce a 16 hour day and 8 hour night in order to germinate the seed and produce plants ready for transfer by April.

The field site consists of two parallel lined cells with controlled inflow and outflow and complete containment. A source of PCE contaminated groundwater lies beneath. Cells are independent and isolated to support controlled experiments. Multi-level transect sampling grids are installed using drive point piezometers manufactured by Solinst Canada. Samples derived from the piezometers monitor initial and developing physical, chemical, and biochemical conditions of the wetland soils as well as contaminant and contaminant breakdown products at multiple depths across the wetland area. Figure 11 shows the sequential phases of construction and demonstrates the distribution of inflow water uniformly within a gravel layer beneath the sediment and the layering of different sediment strata above the water distribution. The final appearance with the installed piezometer grid is also shown. There was considerable concern over maintaining a surface water level during winter freezing conditions. Raising the water level within cell #1 appears to have successfully protected the developing roots of newly planted species by keeping the ice layer raised above the surface. System flow is fully maintained beneath the ice layer with no effect in treatment efficiency.

Figure 11. Sequential Construction of Existing Field Demonstration Cells

a. Excavation forming demonstration cell volume (Cell #2)

b. Protective sand layer and geo-membrane to isolate cell from environment (Cell #1)

c. Inflow pipe distribution within bottom gravel layer – outflow weir box at far end (Cell #2)

d. Installing organic-rich historical wetland soil layer (Cell #2)

e. Initial saturation of Cell #1 (Cell #2 in background)

f. Fully developed wetland plant species in Cell #1 with piezometer grid installed

In addition we observed that the plants planted in the fall of 2000 as well as those planted in the early growing season of 2001 at cells one and two, respectively, grew well and covered the surface with a large biomass. The plant density and the density of duff (decaying, dropped leaves) make the surface of each wetland a suitable location for significant aerobic activity. This activity at the air water and plant-air water interface should be rich in nutrients that support degradation of some of the TCE and other less chlorinated ethenes. The system configuration that holds water a few cm above the surface of this plant and duff rich zone provides a new layer in which this aerobic or microaerophilic activity can proceed.
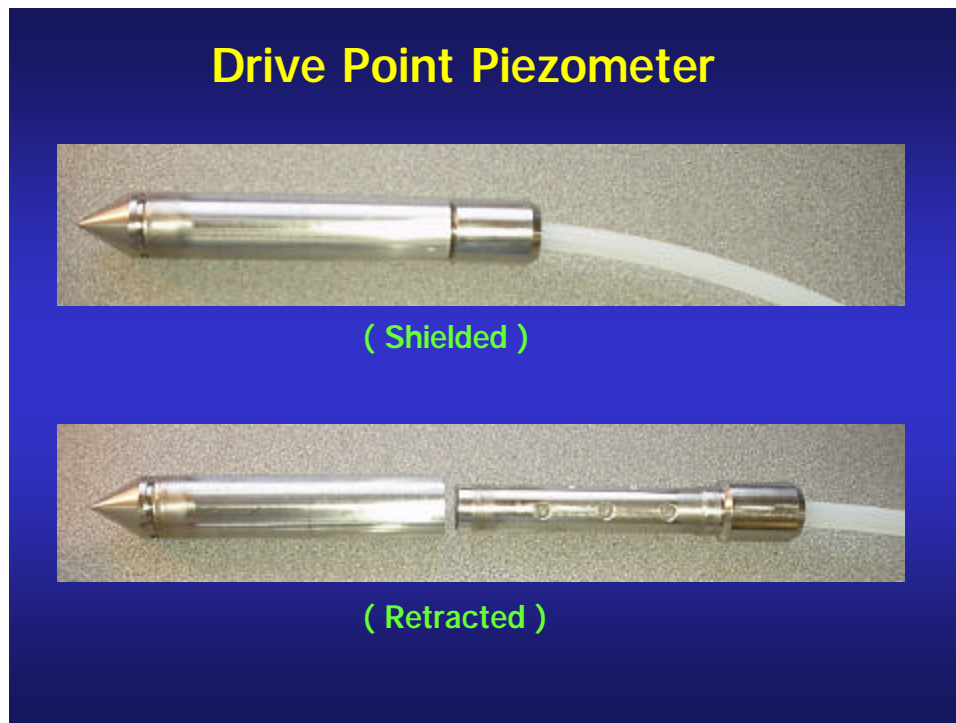
Figure 12. Shielded and retracted piezometer exposing screened area for sampling; Teflon lined tubing attached for sample extraction and head readings.

Figure 12 demonstrates the piezometer configuration. Piezometer screens are shielded for driving into the sediment a few inches below the desired sampling position, then retracted to expose the screened area at the desired sampling depth. Figure 13 illustrates the final placement configuration of each piezometer nest (cluster of piezometers at different depths at one grid location). The 5-inch screened area of the piezometer was placed as nearly as possible in the middle of the respective 18-inch sediment layer. Cell #1 contained 66 nests in a rectangular grid pattern across the cell surface during this study.

Piezometer Installation
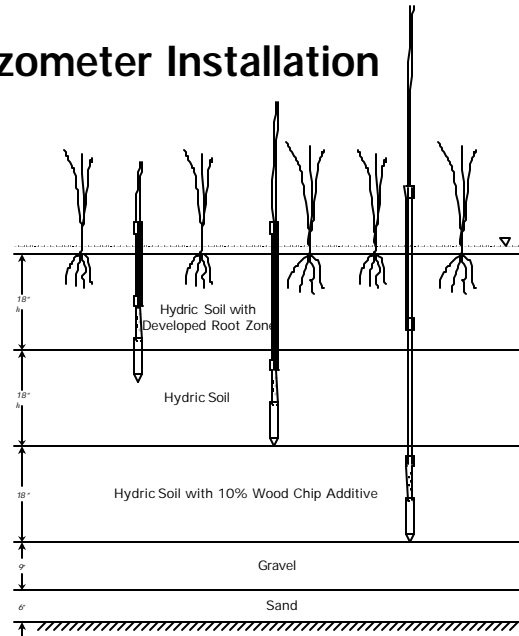
Figure 13. Piezometer nest configuration.

Table 2 shows the configuration of each of the 2 cells constructed in terms of the composition of each sediment layer laid down above the gravel layer with the piping distribution. Only cell #1 is studied here.

Table 2. Composition of the Soil Layers

Layer	Cell 1	Cell 2
Top	Hydric Soil (root zone)	Hydric Soil (root zone)
Middle	Hydric Soil	Local, Iron-rich Fill
Bottom	Hydric Soil (organic matter added)	Hydric Soil

A general schematic of the vertical flow configuration of the cells is given in Fig 14, with uniform water distribution into the gravel layer and weir control device to determine the surface water level. The piezometers were used to take piezometric head readings and to collect samples for chemical analysis in cell #1. Draw-down and recovery tests as well as slug tests were also employed to estimate hydraulic conductivity in the sediment immediately surrounding each piezometer screen. Table 3 gives average head readings from the reference point of the top of the gravel layer beneath the sediment.

43
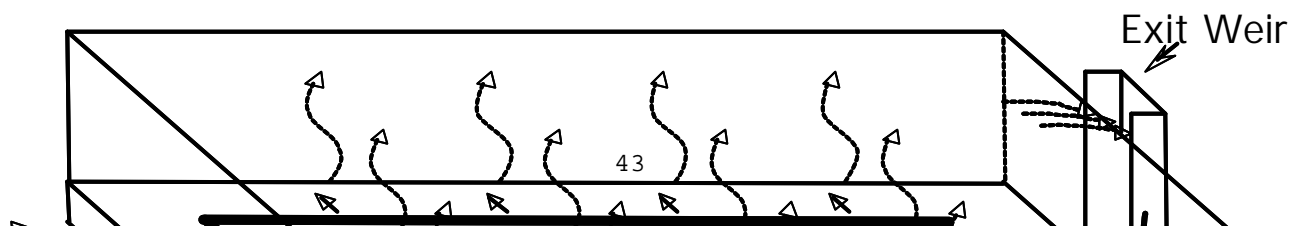
Figure 14. Schematic of vertical flow constructed wetland configuration.

**Table 3. Avg head readings and hydraulic conductivity estimates per sediment
layer.**

Hydraulic Head Readings (arithmetic mean, ft)		Hydraulic Conductivity Estimates (arith mean, ft/sec)		
			Undeveloped	Developed
Top	5.9	Top	$6.4\text{x}10^{-8}$	$8.1\text{x}10^{-6}$ Middle
6.2		Middle	$1.5\text{x}10^{-6}$	$5.6\text{x}10^{-6}$ Bottom 7.6
	Bottom $6.8\text{x}10^{-4}$	$6.8\text{x}10^{-4}$ Bouwer and Rice (1976) (discussed		

below)
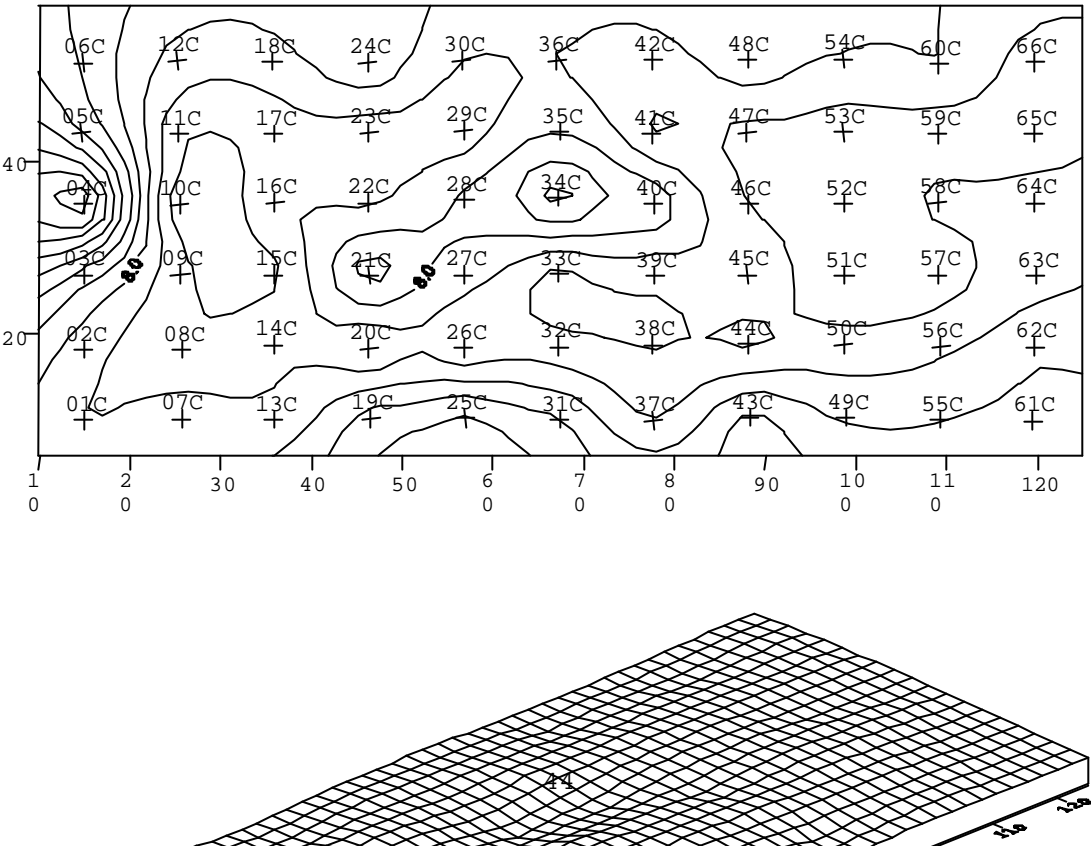
Figure 15. Hydraulic Head: <u>Bottom Soil Layer</u> (11-01-2001)
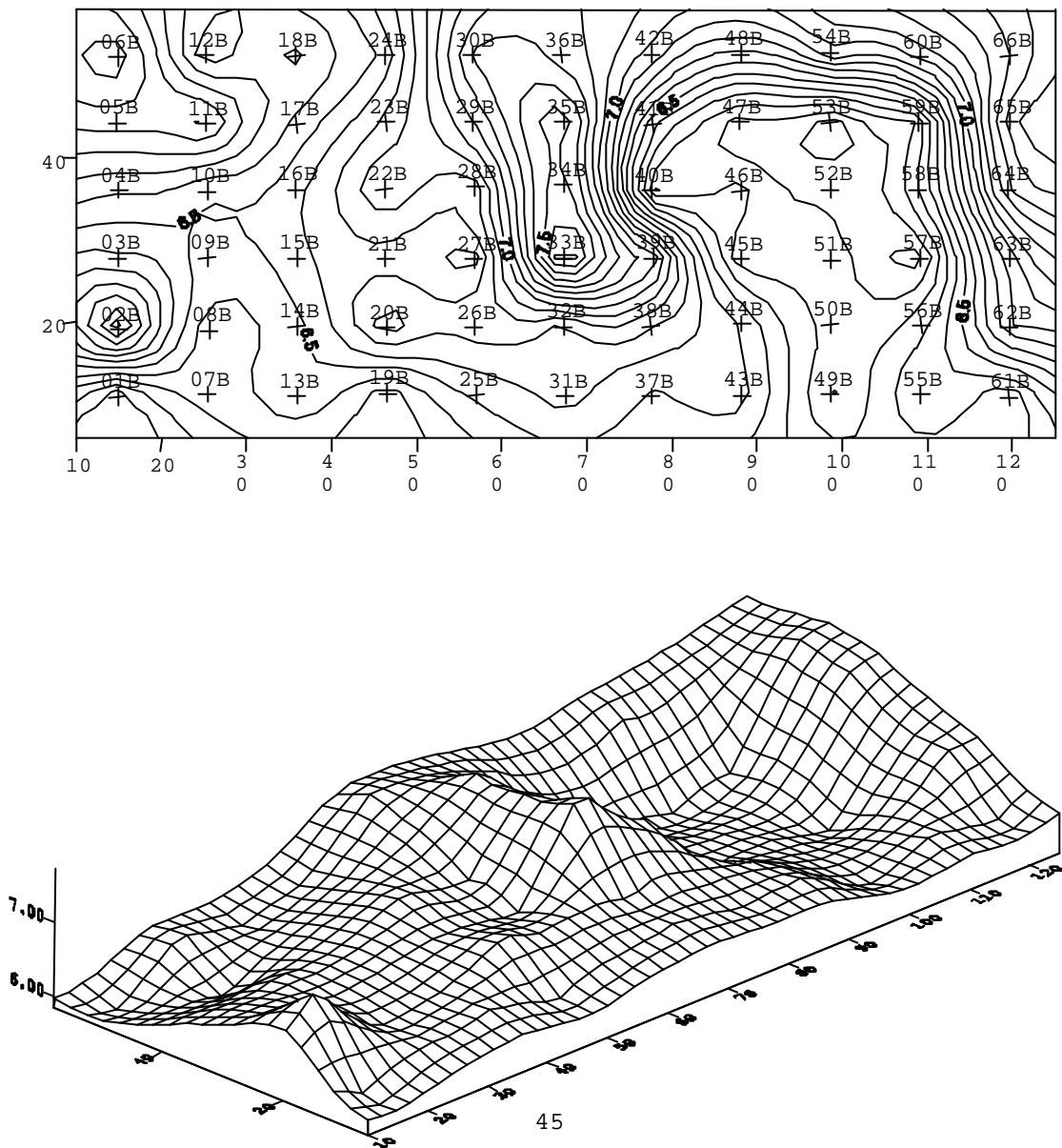
Figure 16. Hydraulic Head: <u>Middle Soil Layer</u> (11-01-2001)
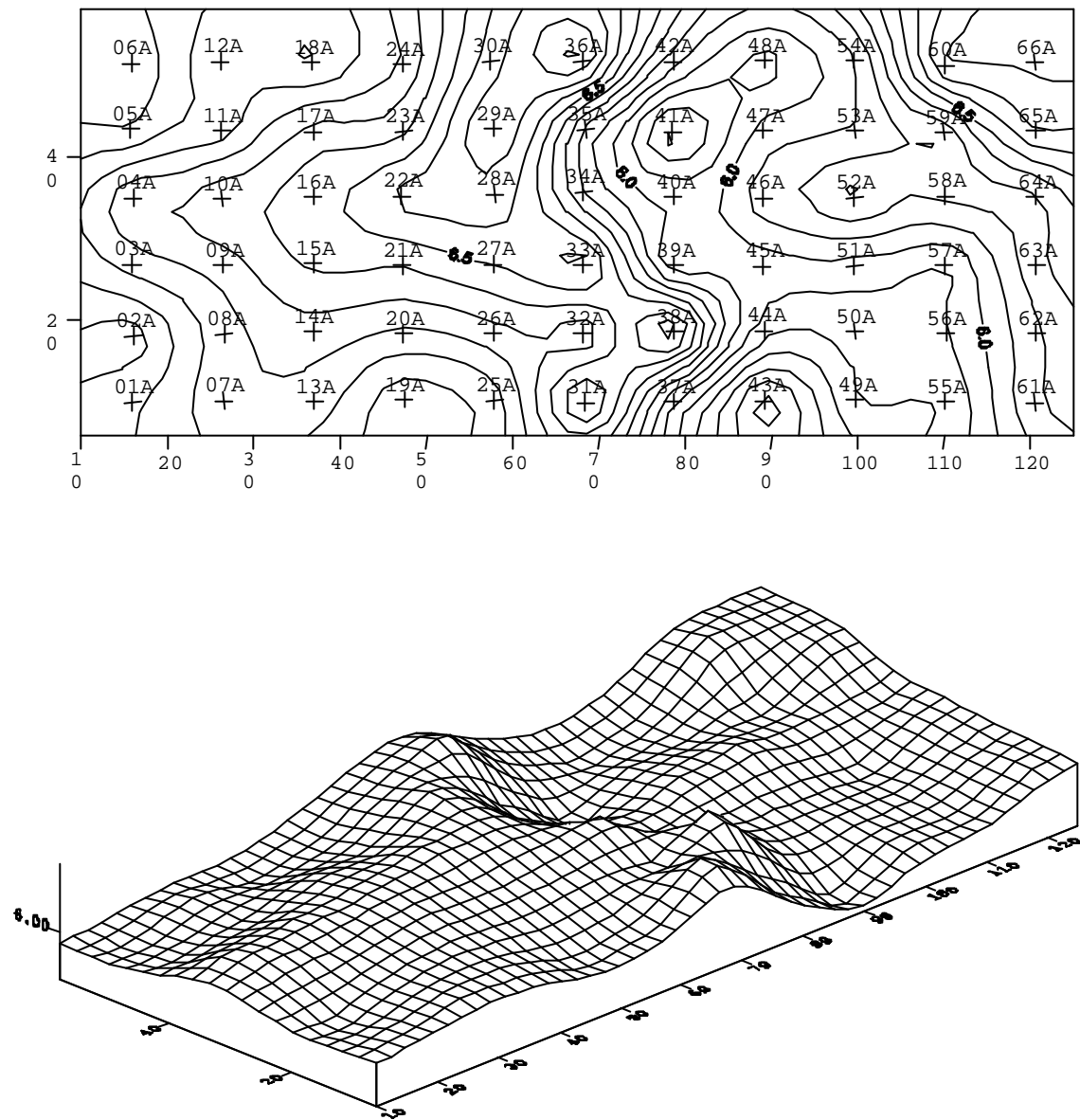
Figure 17. Hydraulic Head: <u>Top Soil Layer</u> (11-01-2001)

<u>Hydraulic Conductivity Estimates</u>: A substantial amount of time and effort was spent conducting hydraulic conductivity tests on the installed grid of piezometers. Analysis using slug test methodology was generally possible for the top and middle layer piezometers due to the relatively low hydraulic conductivities in this portion of the wetland. Slug tests were not a practical means to measure the conductivity of the bottom layer sediments due to the nearly instantaneous rate of water recovery in these piezometers. As a result, pump tests were attempted on a few piezometers to characterize this portion of the wetland.

Slug Tests. The literature is open to interpretation when selecting a relevant slug test for a hydrological setting similar to that of the Wright-Patterson Air Force Base wetland treatment cells. Dawson and Istok (1991) instruct that the Hvorslev (1951) method applies only to confined aquifers while the Bouwer and Rice method is appropriate for unconfined or leaky confined settings.   Although the Wright-Patterson wetland cells, conceptually, represent an unconfined hydrological setting, the presence of a piezometric surface above the surface of the water table mimics the behavior of a confined aquifer system. Similarly, while the Bouwer and Rice method measures the rate of recovery in wells relative to the initial water table elevation, the Hvorslev test measures the rate of recovery relative to the initial potentiometric surface. Finally, the Bouwer and Rice test was intended to test hydraulic conductivity from wells, while the Hvorslev test is normally associated with hydraulic conductivity tests using piezometers. In spite of these concerns, the Bouwer and Rice method was selected for use in this study because the geometry of the piezometer intakes conceptually mimicked that of the Bouwer and Rice test, and an appropriate "shape factor" for use with the Hvorslev method (1951) was not found in the literature until late in study. The observed rate of recovery in this study, therefore, measures the hydraulic head differential from the initial piezometric surface rather than the initial water table elevation. Thompson (1993) also used the Bouwer and Rice test with piezometers to evaluate hydraulic conductivity in a natural wetland.

The Bouwer and Rice slug test – like the Hvorslev test – involves the displacement of a known volume of water in an observation well or piezometer to create a sudden change in hydraulic head; the observed rate of water-level recovery following displacement is related to Darcy's law and can be used to determine the hydraulic conductivity of the media immediately surrounding the intake area of the monitoring device. Like the Hvolslev test, the Bouwer and Rice test can be used on partially penetrating and partially screened wells and piezometers (i.e., wells or piezometers that do not penetrate and are not perforated along the entire saturated thickness of the aquifer). The water for the test can be physically added to or extracted from the piezometer; alternatively, the water can also be displaced by introducing or extracting a solid metal object to produce the necessary instantaneous change in head.

The geometry for the piezometers used in this study is depicted in Figure 18.
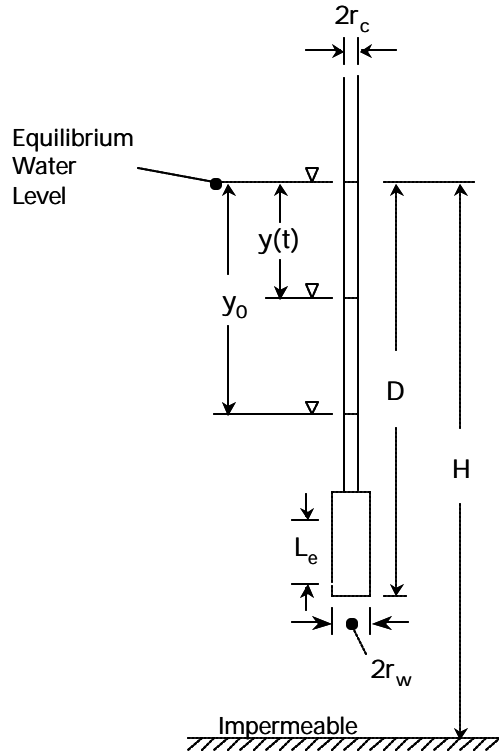
Figure 18. Piezometer Geometry

where

L_e = *effective height of the screened area or perforated zone*
r_w = *radius of the piezometer point or developed zone*
r_c = *radius of the standpipe through which the water level rises/falls*
D = *distance between the equilibrium water level and bottom of the*
    piezometer screen

H = *height of equilibrium water level above the impermeable strata*
y = *water level following displacement from the equilibrium position*

The basic equation to determine hydraulic conductivity using the Bouwer and Rice test is

$$K = \frac{r_c^2 \ \ln(R_e/r_w)}{2 L_e} \ \frac{1}{t} \ \ln\left(\frac{y_0}{y_t}\right)$$

where R_e is the effective radial distance over which the head change is dissipated in the media (Bouwer, 1978).   Bouwer and Rice (1976) present the following equations to compute the value of $ln(R_e/r_w)$:

$$\ln(R_e/r_w)=\left(\frac{1.1}{\ln(D/r_w)}+\frac{A+B\ln\left(\frac{H-D}{r_w}\right)}{L_e/r_w}\right)^{-1}$$

and, if $H=D$,

$$\ln(R_e/r_w)=\left(\frac{1.1}{\ln(D/r_w)}+\frac{C}{L_e/r_w}\right)^{-1}$$

Bouwer and Rice (1976) developed a graph that relates the constants *A*, *B*, and *C* to the known ratio of L_e/r_w. This graph is widely available in many groundwater texts that discuss the test (e.g. Bouwer, 1978; Fetter, 1994; Kresic, 1997). Bouwer and Rice (1976) indicate that the variable $ln((H-D)/r_w)$ has an upper bound of 6 based on the results of analog simulations, so a value of 6 should be used for $ln((H-D)/r_w)$ if the calculated value exceeds 6. Because water flows into or out of the piezometer intake in a predominately radial – rather than vertical – manner, the test primarily yields values of K_H (Bouwer, 1978).

Slug Test Methodology. The tests were conducted by adding or extracting water through the interior ½" Teflon-lined tube. To measure the rate of water level recovery, masking tape was affixed to the outside of the plastic piezometer tube, and the rate of recovery was marked at regular intervals on the tape; the ability to see the water level through the transparent tube greatly enhanced the degree of measuring precision. Hydraulic conductivity values were computed using the above equations. Values for y_0, y_t and *t* were extracted from the straight-line fit of data points on a semi-log plot of *y* versus *t*. Where the data deviated significantly from the theoretical straight line fit (generally for an R^2 of less than 98%), points forming a straight line during the middle portion of the test were used to compute hydraulic conductivity. A total of 64 and 61 slug tests were conducted on the top and middle layer piezometers, respectively; some of these were repeat tests to assess the impact of piezometer development.

Pump Tests. Pump tests were performed on select piezometers in the bottom layer of the wetland to obtain estimates of hydraulic conductivity. (As already noted, the rapid recovery rate of water in the bottom layer piezometers precluded the use of slug tests to characterize hydraulic conductivity in this portion of the wetland.) Where feasible, pump tests are often preferred over slug tests to obtain in-situ estimates of hydraulic conductivity because they evaluate a much larger region of soil.

The majority of the pump tests presented in the literature involve observations of water level (or potentiometric surface) decline in wells or piezometers as another well is pumped, normally at a constant rate. When water is pumped out of a well, a cone of depression forms in the water table (or potentiometric surface) and expands outward from the well until a recharge boundary is reached. Analytical equations that compute hydraulic conductivity from the drawdown once this *steady-state* condition is reached are straightforward but require wells that fully penetrate the aquifer. An analysis of *transient*

time-drawdown data is necessary for wells that only partially penetrate an aquifer as well as for tests that do not reach steady state conditions.

Various methods for analyzing transient time-drawdown data from aquifer pump tests exist in the literature. Many employ a *curve-fitting* technique that compares the transient time-drawdown data obtained from the test with the plot of a theoretical *type-curve*. In addition to the extent of well penetration, the type of aquifer (confined, leaky, or unconfined) also influences the choice of an appropriate test for transient conditions. Dawson and Istok (1991) provide a useful summary of aquifer tests that are applicable over a wide range of geological settings.

The piezometers installed in wetland cell number one only partially penetrate the soil layer of interest, and by design the hydrogeologic setting is conceptually that of an unconfined aquifer. The appearance of transient time-drawdown data collected during the pump tests, however, mimicked that of a confined, leaky aquifer with influence from a source bed (i.e., an aquifer with an overlying *confining* layer that is permeable enough to transmit water down into the aquifer from a constant source of recharge) as illustrated by Dawson and Istok (1991). Fetter (1994) cautions that the effects of partial penetration can produce a time-drawdown curve that appears similar to that for a confined, leaky setting, but he also considers an aquifer *confined* when it is overlain by strata with a conductivity that is two orders of magnitude less than that of the aquifer of interest. The evidence supporting confined and leaky conditions (rather than unconfined) for the bottom soil layer of the wetland was two-fold. First, the water level recovery observed for slug tests attempted in the bottom layer was considerably faster (virtually instantaneous) compared to that for tests conducted in the top two layers of soil indicating a hydraulic conductivity much higher than that above. Second, the pump tests measured the decline of the potentiometric surface – rather than a declining water table - which again is consistent with a confined aquifer setting.

Table 4 gives mean organic acid concentrations in each layer, indicating a level of microbial activity beginning to develop.

Table 4. Organic Acid Mean Concentrations across Soil Layers (ppb).

|	C4 Butyrate	C3 Propionate	C3 Lactate	C2 Acetate	C Formate
Top	100	56	52	2796	205
Middle	227	29	209	773	236
Bottom	24	1	95	4525	19

These mean concentrations are difficult to interpret in the aggregate. An order-of-magnitude increase in butyrate concentration from the bottom to the middle layer could simply indicate the longer residence time of a parcel of water in the middle layer, accumulating the effects of on-going breakdown of organic material resident in the

sediment. On the other hand, C_{3-4} organic acids could be depressed in the bottom layer due to apparent high acetogenesis. The lower acetate concentration in the middle layer could also suggest some methanogenesis developing within the system, conditions associated with the highly reducing environment needed for reductive dechlorination. Drawing such conclusions from these mean data across layers, however, must be done in light of the high degree of heterogeneity within each layer as shown in Figures 19 and 20. These figures reveal concentrations of butyrate ranging from near 0 to 300 ppb and of acetate from 0 to 5 ppm in a single sediment layer, suggesting that microbial consortia are still in a state of development throughout the wetland cell even after a year of operation. Another year of data will reveal the speed of development and allow preliminary conclusions for seeding such systems or speeding their microbial development.

Of primary interest is the change in chlorinated ethene concentrations from bottom to top of the cell. Figures 21 through 23 show both the PCE and TCE contours in each sediment layer, again demonstrating significant heterogeneity. On average, as shown in Table 5, there is significant reduction of PCE from bottom to top with slightly increasing TCE. The table shows inflow and outflow concentrations as well. The elevated outflow concentration above that seen in the top sediment layer is attributed to short circuit flow in isolated portions of the cell (a pocket of fluidized sediment is observed) and along the geomembrane at the walls of the cell. No DCE, vinyl chloride, or ethene/ethane can be detected even though the method should be able to see it if it is there. As yet, there is no mass balance analysis available to demonstrate the fate of the influent PCE.

Figure 23 does, however, present some evidence of reductive dechlorination in that areas observed to have significantly lower PCE demonstrate elevated TCE in the same locations. This is even more striking when comparing PCE contours to nitrate contours as in Figure 24. Since nitrate, flowing into the system at about 3 ppm, would out compete PCE as an electron acceptor, reductive dechlorination would be inhibited in the presence of nitrate, and, inversely, reductive dechlorination would be enabled in locations
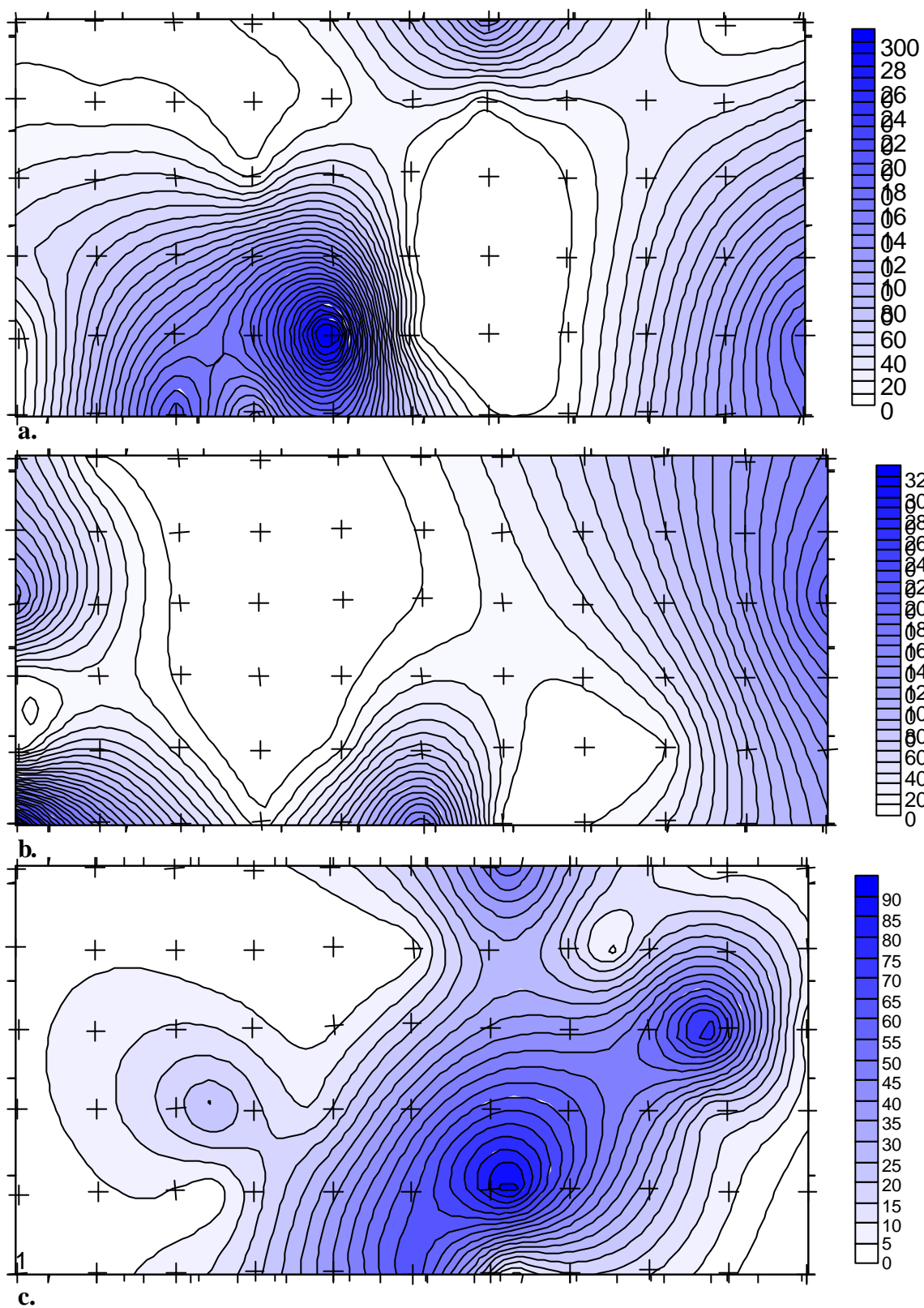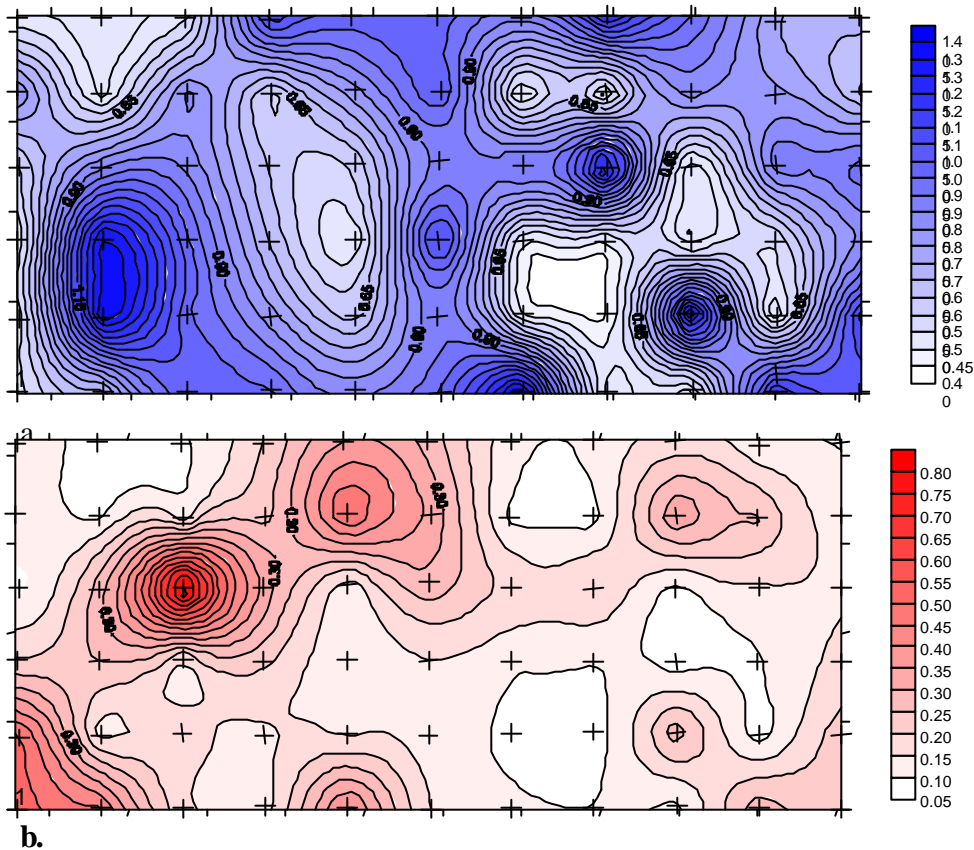
Figure 19. Butyrate concentration contours (ppb) in the 3 sediment layers of the constructed wetland one year after initiating the system flow. a) top layer; b) middle layer; c) bottom layer.

a.

b.
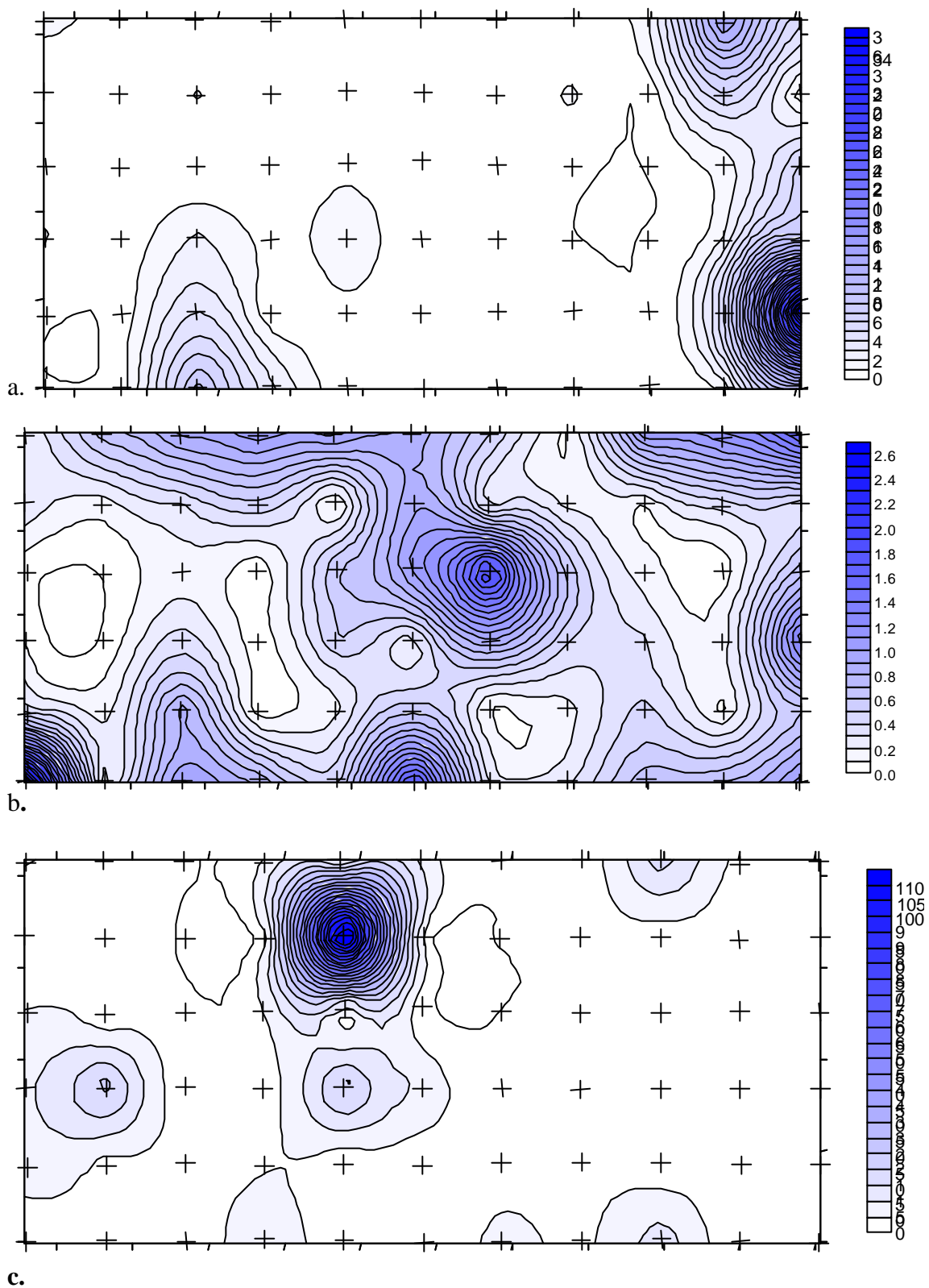
c.

Figure 20. Acetate concentration contours (ppm) in the 3 sediment layers of the constructed wetland one year after initiating the system flow. a) top layer; b) middle layer; c) bottom layer.

of low nitrate. This suggests that quick consumption of nitrate (by addition of easily assimilated organic material in the influent, for example) could potentiate reductive dechlorination. Table 6 summarizes the mean concentrations of other inorganic ions found in the wetland sediments.

Figure 21. PCE (a) and TCE (b) concentration contours (ppb) in the top layer of the constructed wetland sediment.
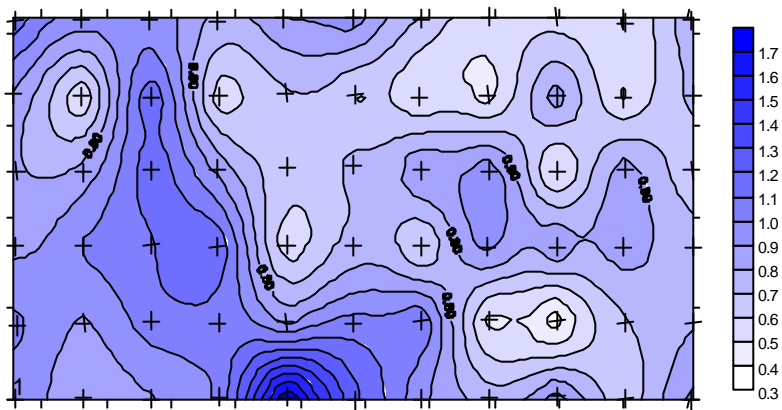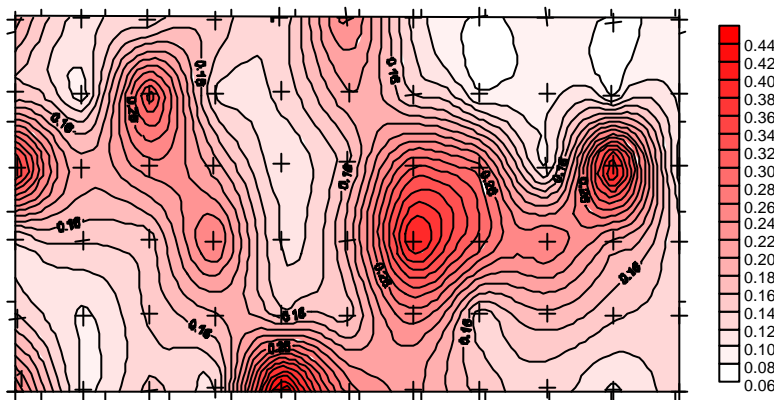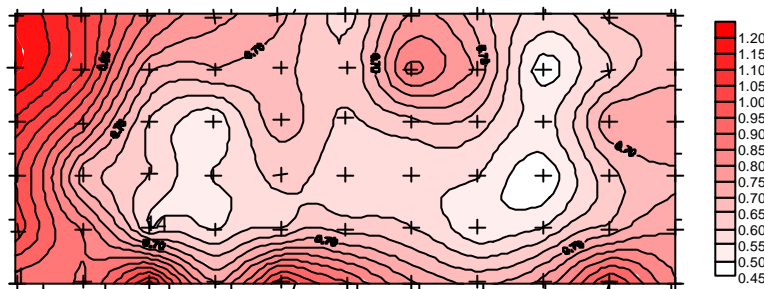
Figure 22. PCE (a) and TCE (b) concentration contours (ppb) in the middle layer of the constructed wetland sediment.
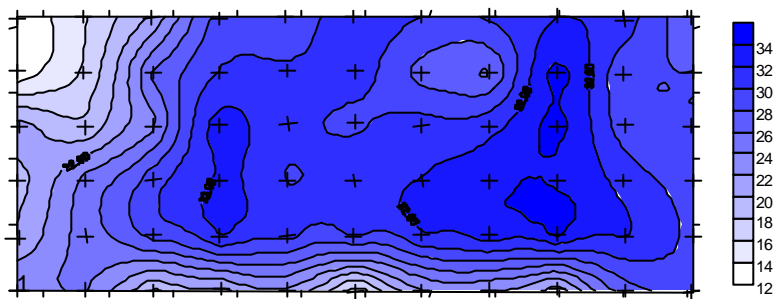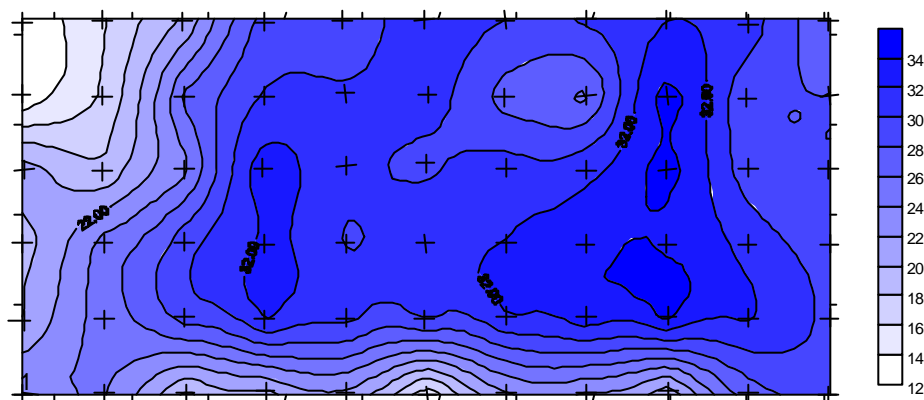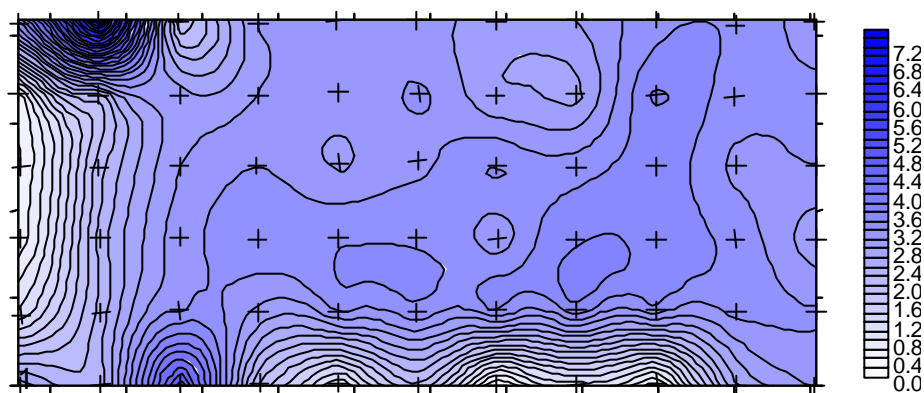

Figure 23. PCE (a) and TCE (b) concentration contours (ppb) in the bottom layer of the constructed wetland sediment.

Table 5. PCE and TCE Mean Concentrations across Soil Layers (ppb).

	PCE	TCE
Outflow	5.8	2.4
Top	0.8	0.2
Middle	0.8	0.2
Bottom	27.0	0.7
Inflow	34.0	0.6

a. PCE

b. Nitrate

Figure 24. Comparison of a) PCE (ppb) and b) nitrate (ppm) concentration contours in the bottom layer of wetland sediment, suggesting nitrate inhibition of reductive dechlorination.

Table 6. Inorganic ion Mean Concentrations across Soil Layers (ppb).

	Nitrate	Sulfate	Chloride	Fluoride
Top	15,623	15,908	82,536	167
Middle	15,476	12,334	65,948	191
Bottom	3,592	50,043	80,958	156

The following conclusions can be drawn from the wetland studies in both the laboratory and after one year of operation at the field scale:

1. Construction techniques must be refined to promote isotropic soil conditions for uniform flow and prevention of short circuiting.

2. Significant fermentation including acetogenesis develops quickly within anaerobic zones of historical wetland sediment.

3. PCE can initially be significantly reduced from inflow to outflow in an upward flow constructed wetland system. The mechanism for this reduction is not fully established, and no mass balance analysis has elucidated the complete fate of influent PCE. No degradation products are found below TCE.

4. Laboratory results confirm the design concept of reductive dechlorination followed by aerobic oxidation of chlorinated aliphatics. Results also suggest a much stronger role for phytoremediation in these systems.

PUBLICATIONS AND PRESENTATIONS FROM THE CURRENT WORK

Publications.

Christ, J.A. and M.N. Goltz, Contain and Destroy, The Military Engineer, 31(611):55-56, 2001.

Ferland, D.R. and M.N. Goltz, Modeling Innovation, The Military Engineer, 31(610):45-47, 2001.

Ferland, D.R., K.G. Boggs, S. Niekamp, J.A. Christ, A. Agrawal, and M.N. Goltz, Chlorinated hydrocarbon treatment using a horizontal flow treatment well system, Physical and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds, G.B. Wickramanayake and A.R. Gavaskar, Eds., pp. 253-260, Battelle Press, Columbus, OH, 2000.

Ferland, D.R., In Situ Treatment of Chlorinated Ethene-Contaminated Groundwater Using Horizontal Flow Treatment Wells, MS Thesis, AFIT/GEE/ENV/00M-05, Graduate School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB OH, March 2000.

Fernandez, M., Optimization of Palladium-Catalyzed In Situ Destruction of Trichloroethylene-Contaminated Groundwater Using a Genetic Algorithm, MS Thesis, AFIT/GEE/ENV/01M-02, Graduate School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB OH, March 2001.

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Campbell, J.S., A Comparison Of Modeling Approaches In Simulating Chlorinated Ethene Removal In A Constructed Wetland By A Microbial Consortia, MS Thesis, AFIT/GEE/ENV/02M-02, Graduate School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB OH, March 2002.

Bugg, B.M., An Anion Characterization Of A Constructed Wetland Used For Chlorinated Ethene Remediation, MS Thesis, AFIT/GEE/ENV/02M-01, Graduate School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB OH, March 2002.

Submitted Publications.

Stoppel, C.M. and M.N. Goltz, Modeling Pd-Catalyzed Destruction of Chlorinated Ethenes in Groundwater, Journal of Environmental Engineering, submitted 2002.

A manuscript based on the work completed is under submission to Environmental Science & Technology that summarizes the results of investigations thus far about

reaction products and pathways of chlorinated ethene degradation in in-well metal catalyst reactors.

Another manuscript based on the results from column investigations is under preparation, summarizing the effect of flow and inorganic solutes on the reaction kinetics in a model system.

Construction of the field wetland demonstration and results from initial sediment water sampling indicating treatment efficiency is in preparation for the Journal of Environmental Engineering.

Presentations.

Ferland, D.R., K.G. Boggs, S. Niekamp, J.A. Christ, A. Agrawal, and M.N. Goltz, Chlorinated hydrocarbon treatment using a horizontal flow treatment well system, The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey CA, 22-25 May 2000.

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A poster titled "In situ groundwater treatment using Pd-catalysts and horizontal flow treatment wells" was presented at the Partners in Environmental Technology Symposium and Workshop, Arlington VA, 28-30 November 2000.

Slusser, Amon, Shelley, Goltz, and Agrawal, "Dechlorination potential of wetland soils for treatment of contaminated groundwater", Sixth International Conference on In Situ and On-Site Bioremediation, San Diego CA, 4-7 June 2001

Guin, Slusser, Shelley, and Agrawal, "Field-scale bioremediation of chlorinated ethenes in constructed wetland bioreactors", Sixth International Conference on In Situ and On-Site Bioremediation, San Diego CA, 4-7 June 2001

A technical oral presentation on the effect of flow and inorganic solutes on the reaction kinetics in a model system was made at the National Groundwater Association's Thesis Conference in Jackson Hole, Wyoming.

Goltz, M.N., et al., Application of Circulating Wells for In Situ Treatment of Contaminated Groundwater, International Symposium on Soil and Groundwater Contamination Control Strategy, Kyung Hee University, Seoul, Korea, 21 June 2001.

Mark Goltz presented the modeling work on in-well metal catalyst treatment of chlorinated ethenes on 16 Jul at the Kyonggi Environmental Technology Center seminar, Kyonggi Province, Korea.

Submitted Presentations.

Two extended abstracts of the completed work have been submitted to the American Chemical Society's national meeting for both oral and poster presentation.

Stoppel, C.M., A. Agrawal, and M.N. Goltz, A model for Palladium catalyzed destruction of chlorinated ethenes in groundwater, The Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey CA, 20-23 May 2002.

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14. ABSTRACT

This work explores two innovative technologies for the remediation of chlorinated ethene solvents contaminating groundwater: 1) groundwater circulation wells (GCWs) with downwell zero-valent metal reductive dechlorination reactors and 2) constructed vertical subsurface flow wetlands. Both the natural dechlorination in wetland sediments, and the engineered dechlorination in a well using zero-valent metals have major implications for the treatment of Air Force pollutants, with the potential to save millions of dollars annually in long term remediation at hundreds of sites across the Air Force. Complementary modeling and column studies examined the potential for controlling and treating groundwater contamination using groundwater circulation wells (GCWs) with downwell zero-valent metal reductive dechlorination reactors. The construction of the field scale wetland research facility includes two complete wetland cells (140x60 feet each), fully contained. Chemical analysis of samples drawn from the various depths of wetland sediment suggests a very heterogeneous development of microbial activity relevant to reductive dechlorination over the course of one year of operation. Concentration contours of PCE, TCE, and nitrate suggest that reductive dechlorination is taking place when more readily reducible electron acceptors (like nitrate) are depleted. PCE is reduced ten-fold from inflow to outflow, even with significant short-circuiting of flow from the bottom sediments to the outflow. Data suggests 100-fold treatment is possible.

15. SUBJECT TERMS

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